

KINETIC ASPECTS ON THE GASIFICATION OF BLACK SHALE FROM THE RANSTAD DEPOSIT

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HANS EKLUND

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Abstract The conditions of <u>gasification</u> at atmospheric pressure of <u>black shale</u> from the Swedish Ranstad deposit have been studied. The experiments were carried out in <u>bench scale</u> fluidized bed reactors and by <u>thermogravimetry</u>. <u>Kinetic</u> parameters for the steam-carbon and the carbon dioxide-carbon systems were obtained by fitting experimental data to <u>Langmuir-Hinshelwood type equations</u>, including also the effects of product gas retardation. The kinetics of the heterogeneous <u>shift reaction</u> over shale char and kerogen free ash were studied in a differential reactor. <u>Mathematical models</u> for an oxygen blown <u>fluidized bed</u> reactor and an airblown circulating fluidized bed were developed. Results of <u>scale-up simulations</u> are presented.		
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KINETIC ASPECTS ON THE GASIFICATION OF
BLACK SHALE FROM THE RANSTAD DEPOSIT.

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This thesis consists of this summary and the following papers referred to in the text by Roman numerals.

- I. Bjerle I., Eklund H., Svensson O.
"Gasification of Swedish Black Shale in the Fluidized Bed;
Reactivity in steam and carbon dioxide atmosphere."
To be published in the July 1980 issue of Ind. Eng. Chem., Process Des. Dev.
- II. Berggren J-C., Bjerle I., Eklund H., Karlsson H., Svensson O.
"Application of Chemical and Physical Operations in a Circulating Fluidized Bed Reactor. Part 1: Gasification of uranium bearing black shale."
Published as a shortened version in Chem. Eng. Science, vol 35, no 1-2 (1980), p 446-455.
- III. Bjerle I., Eklund H., Linné M., Svensson O.
"Thermogravimetric Analysis of Swedish Shale Char; Kinetics of the steam-carbon and carbon dioxide-carbon reactions."
Submitted for publication.
- IV. Eklund H., Linder G., Svensson O.
"A Kinetic Study of the Heterogeneous Shift Reaction over Shale Char and Kerogen Free Ash."
Report, Dept. of Chemical Engineering, Lund Institute of Technology, April 1980.
- V. Eklund H., Svensson O.
"A Reactor Model for the Gasification of Black Shale in the Fluidized Bed."
Report, Dept. of Chemical Engineering, Lund Institute of Technology, April 1980.

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1. INTRODUCTION

The deposits of Cambrian black shale in the central parts of Sweden are one of the largest reserves of uranium in Europe. Besides uranium, the shale contains recoverable amounts of both kerogen, and metals such as K, Al, V, Mo. Although the uranium in the shale from the Ranstad deposit is the primary product, the other species are considered for recovery in a combined thermal and hydro-metallurgical process.

For the utilization of the kerogen, the gasification route has been proposed, and this is primarily due to a low oil yield by pyrolysis (1.5 wt-%) and a high sulphur content (7 wt-%). The large scale nature of shale processing makes the fluidized bed reactor suitable for the gasification step. One severe disadvantage however, is the scale-up procedure of fluidized beds. Because of the complex hydrodynamics of the gas phase and to some extent the solids, the extrapolation of small scale results is uncertain.

The first basis for the development of scale-up models is a good knowledge about the rate controlling steps in the process. In the gasification case, where the chemical reaction step has been shown to be rate controlling, data on chemical kinetics are essential.

This summary deals with the kinetic aspects of the gasification of Ranstad shale and gives some outlines of how the data can be used in predicting the performance of a large scale reactor.

2. CHARACTERIZATION OF THE RANSTAD SHALE

The Swedish shale deposits date back to the Cambrian era, when they were formed by sedimentation in shallow brackish or fresh water. The shale consists mainly of a flaky clay structure, in which organic matter, kerogen, is embedded. Small aggregates of pyrite, some microns in size, are dispersed throughout the organic structure.

The inorganic part of the Ranstad shale, which is 70 to 75% by weight, is built up by a silica network of different illites and feldspars. The kerogen content, between 15 to 25%, varies throughout the seam, whereby the level of maximum uranium content does not exactly correspond to that of maximum kerogen. In the fraction of the seam that is of interest to recover, the uranium and kerogen content is about 0.03% and 20% respectively. Small amounts of so-called kolm are distributed as very thin lenses. The kolm is highly enriched in both uranium and kerogen. Kolm samples with up to 0.7% uranium and 70% organic carbon have been found. The origin of the uranium enrichment in the shale is not fully understood. One plausible theory is that the uranium was precipitated as tetra valent uranium oxide or uranite by hydrogen sulphide, present in the acidic and reducing water environment. The uranium was then built into the sediments of decaying organic matter (1). Also distributed in the shale seam are lenses of limestone representing about 5% of the seam by weight. The shale used in the gasification tests has been cleaned to a residual limestone content of about 1.5%.

An ultimate analysis of the shale and a Fischer assay is given in Table 1a and 1b below.

	raw shale, mf	kerogen, maf
% C	15.0	73.7
% H	1.4	6.9
% O	1.7	8.5
% N	0.4	1.9
% S	7.0	9.0
Calorific Heat of Combustion (MJ/kg)	6.6	27.0
Molar formula, kerogen; $C_1 H_{1.12} O_{0.09} N_{0.02} S_{0.05}$		

Table 1a: Ranstad shale, ultimate analysis

Table 1 continued:

Gas	35	kg/ton
Oil	15.5	"-
Water	5.5	"-
Residue	944	"-
Fischer yield	16.3	l/ton
API-Index (oil)	16.1	

Table 1b: Fischer assay

From the Fischer assay an oil yield of only 1.5% can be stated. According to Swanson (1) and Dow (2), the occurrence of two different types of kerogen is known; saprophelic kerogen of algaecic origin, giving high oil yields, and humic kerogen, predominately plant derived, with a low oil yield. The structure of the humic kerogen is assumed to be highly aromatic, with the side chains predominantly built up from short aliphatic hydrocarbons. With this approach not only the low oil yield but also the relatively large amounts of methane and light hydrocarbons evolved during pyrolysis of Ranstad shale can be explained.

From Figure 1, where the molar ratio of H/C is plotted against the ratio O/C, the relationship of Ranstad shale with bituminous and sub-bituminous coals is stated. The highly volatile Boghead and Cannel coals show similarities with shales because in contrast to other coals, they have a very regular organic structure. The volatile matter content of Ranstad shale kerogen, 40 - 45% is also in accordance with that of volatile coals.

On the other hand, for Närke shale marked with the N in Figure 1, an oil shale character is more obvious, as seen both from the figure and also from an oil yield of 7-8% (~20 US gallon/ton).

Thus, it can be concluded that the Ranstad shale is not to be looked upon as an oil shale, but more as a highly volatile coal with an extreme ash content.

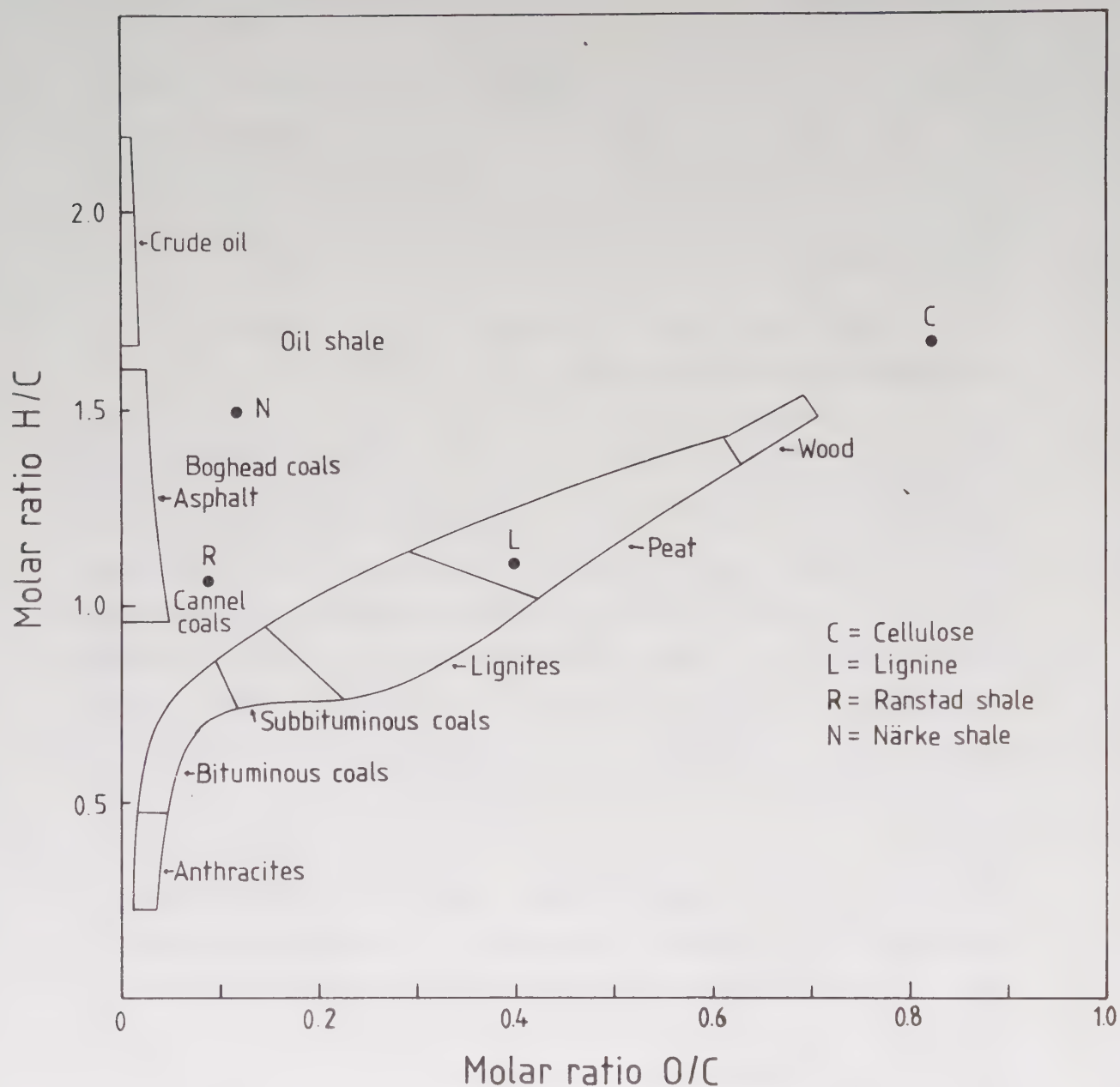


Figure 1.

Comparison of elementary analysis between Swedish shales and coals. Molar ratio H/C vs. molar ratio O/C. Figure originally taken from Meunier (3).

3. SUMMARY OF THE PAPERS I TO IV

In the following, the experimental findings and the kinetic data obtained will be summarized. The work conducted can be roughly subdivided into four phases:

- o Gasification of shale in an externally heated bubbling fluidized bed. The main reason for building this reactor was to get a preliminary indication of the feasibility of gasifying Ranstad shale. Additionally, kinetic data from a fluidized bed reactor could be obtained. (Paper I, Section 3.1 of Summary).
- o The development of an air blown circulating fluidized bed gasifier. With this reactor, the principle of using the shale char as a circulating heat carrier between a heat generation and a gasification zone was demonstrated. Furthermore, a reactor concept, where the solid material circulation was maintained without moving part control could be shown in operation. (Paper II, Section 3.3 of Summary).
- o Special investigations to study, the retarding properties of H_2 and CO on the gasification rate, the catalytic effects of impregnating the shale char with alkali metal salts, and the kinetics of the heterogeneous shift reaction over shale char. (Paper III, IV, Sections 3.2 and 3.4 of Summary.)
- o The utilization of the kinetic parameters in the development of a reactor model for scale-up simulations. (Paper V, Section 3.6 of Summary.)

3.1. BUBBLING FLUIDIZED BED REACTOR

3.1.1. Initial tests

The intervals for stable fluidization were investigated in both cold and hot runs in air and steam respectively. It was shown that superficial velocities 1.5 - 2 times the minimum fluidization velocity could be used. A sieve analysis of the shale and bed char is given in Table 4, paper I. With steam as the fluidizing gas at temperatures of 700 - 900°C, the superficial gas velocities used were between 1 to 1.5 m/s.

In heterogeneous reaction systems as the fixed carbon gasification, the reaction rate is controlled by different mechanisms in different temperature intervals. In coal gasification, the chemical kinetics are the rate controlling step, but due to the high ash fraction, an intra-particle mass transfer resistance could not be excluded a priori. Different methods of investigation were used, coarse and fine shale particles were gasified under identical conditions in a differential reactor and the rates were compared, the bed mass from the fluidized bed was screened and analyzed with respect to carbon content, and finally the effectiveness factor of a shale particle was theoretically calculated. In all cases the mass transfer influence could be neglected, which can also be observed from Figure 2, where the experimental gasification rate is compared with curve forms typical for pore and gas film diffusion control. Thus, with the chemical reaction control, the gasification of the fixed carbon can be treated kinetically as a pseudohomogeneous volume reaction.

3.1.2. Gasification in H₂O and CO₂ atmosphere

Gasification tests with H₂O and CO₂ pressures of 90 to 100 kPa have been performed between 650 and 850°C, and char residence times from 0.5 to 2 hours with H₂O and 1 hour with CO₂. The reasons for the chosen temperature limits were primarily related to apparative limitations, but were also due to a temperature restriction in a proposed metallurgical

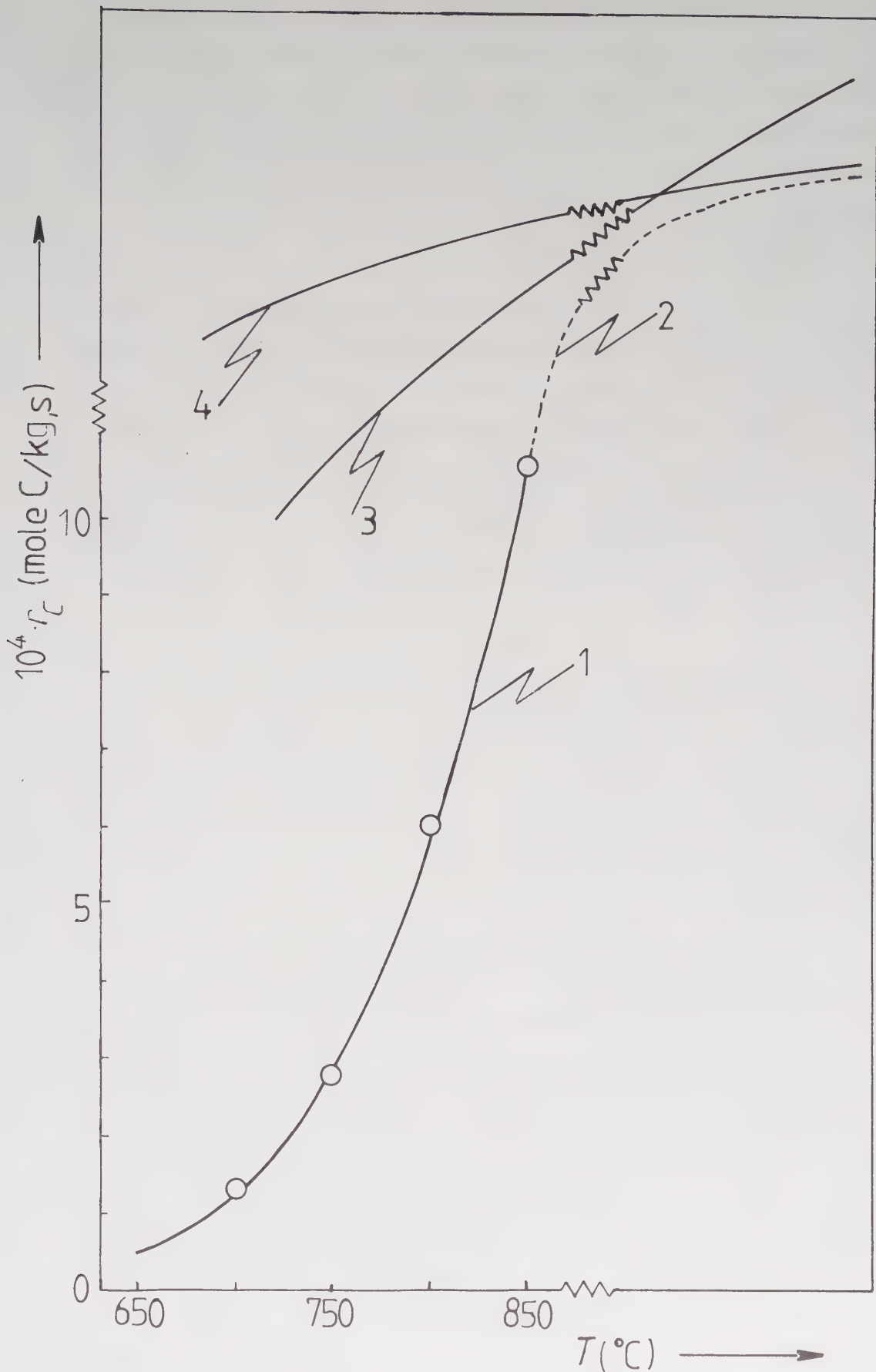


Figure 2.

Gasification rate vs. temperature at 1 h char residence time.

Line 1: Experimental rate.

Line 2: Chemical reaction control.

Line 3: Pore diffusion control.

Line 4: Gas film diffusion control.

processing of the shale. As far as residence times are concerned, the limits are given by a compromise between reasonable magnitudes of carbon conversion and reactor size in the technical application. In Figure 3, the carbon conversion including the pyrolysis contribution is shown for steam and carbon dioxide gasification. It should be observed that the reactor is externally heated, and thus the carbon conversion in an autothermal process will be higher.

While the main purpose of the work has been to study the fixed carbon reactions, the pyrolysis process has been studied only briefly. In steady state runs with H_2O , the yields of pyrolytic hydrocarbons and sulphur compounds are almost unaffected by temperature. The pyrolytic gas production expressed as mole/kg shale feed is given in Table 2 below. A slight influence of the char residence time could be seen, and the upper limit of the standard deviation values in Table 2 should be preferably used for residence times exceeding 1 hour, and the lower values for shorter times than 1 hour.

Gas	mole/kg shale feed
CH_4	0.66 ± 0.11
C_2H_4	0.13 ± 0.08
$\Sigma C_2H_6, C_2H_2$	0.04 ± 0.02
C_3H_n	0.06 ± 0.03
H_2S	0.85 ± 0.23
COS	0.004 ± 0.002

Table 2: Yield of pyrolytic compounds by steam gasification.

When operating the fluidized bed with pure H_2O or CO_2 , the partial pressures of these remain almost constant due to the large excess of gas necessary for stable fluidization. The bed can therefore be considered as a differential unit on the gas side, and the reaction rate of fixed carbon can be described by a simple first order equation;

$$-(r_C) = -k_0 e^{-E_A/RT} \cdot c_C \quad (1)$$

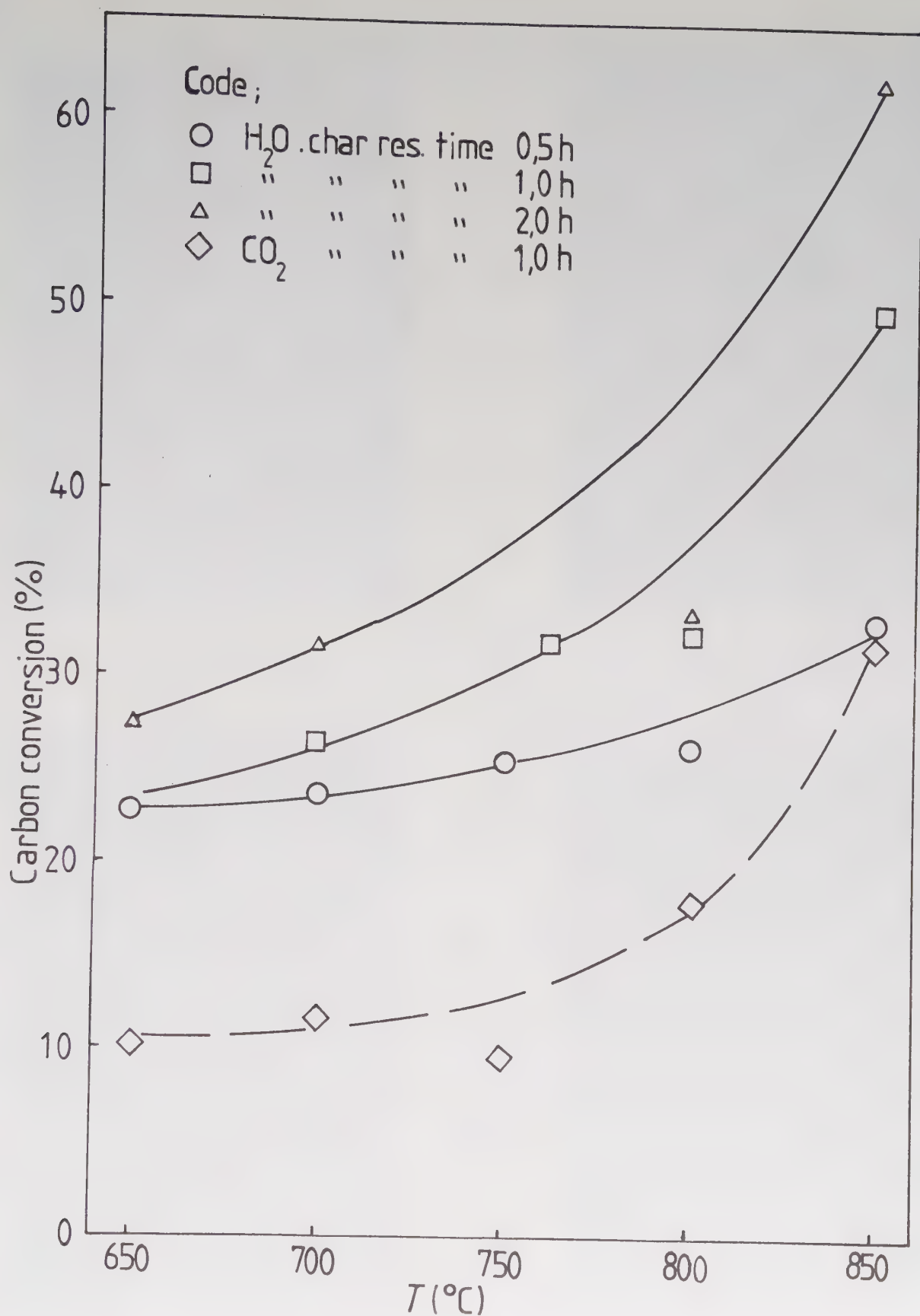


Figure 3.

Carbon conversion vs. temperature. Alloterm steam and carbon dioxide gasification.

Kinetic parameters were obtained by fitting the experimental data from runs in H₂O and CO₂ atmospheres to equation (1). (section 4.2, paper I).

The kinetic data are summarized in Table 3.

Atmosphere	Preexponential factor k_0 (s ⁻¹)	Apparent Activation Energy E_A (KJ/mole C)
H ₂ O	1000	147
CO ₂	8780	171

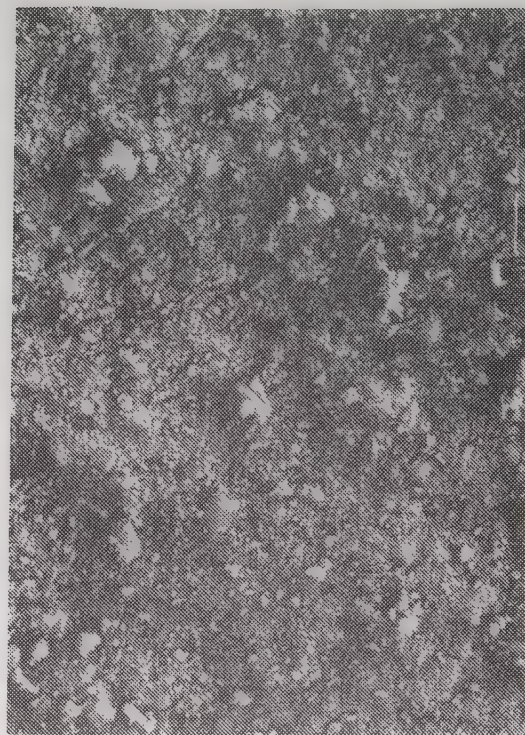
Table 3: Kinetic parameters by H₂O and CO₂ gasification
Reaction pressure: 90 to 100 kPa

The physical changes of the shale during gasification have been studied by measuring the BET-area and by examination of chars in a scanning electron microscope. The change of the BET-area with increasing carbon conversion is given in Figure 9 of paper I. The native shale has a low BET-area of about 2 m²/g, which is increased during the pyrolysis process by a factor 20. With decreasing carbon content in the char, an almost linear decrease of the BET-area down to nearly the same specific surface as for the native shale could be observed.

In Figures 4 a-d, SEM-photos of shale, and different chars are shown in 3000 x magnification. The pictures do not display any conclusive differences, in spite of their broad spectra of gasification conditions. Furthermore some examinations were performed at 30000 x magnification, but gave no additional information. The strong increase in BET-area previously described is to be related to an increase of the micro-porous structure also within the particle which can not be discovered in the photos.



a) Natural shale, BET area $2.2 \text{ m}^2/\text{g}$.



b) N_2 -pyrolyzed char, 850°C ,
6 h, BET area $14 \text{ m}^2/\text{g}$.



c) N_2 -pyrolyzed char, 500°C ,
3 h, BET area $51 \text{ m}^2/\text{g}$.



d) H_2O -gasified char, fluidized bed,
 840°C , 1 h, BET area $19 \text{ m}^2/\text{g}$.

Figure 4.

SEM-photos of Ranstad shale and gasified chars, 3000x magnification.

3.1.3. Gasification in H_2O/N_2 and CO_2/N_2 mixtures

The dependence of the reaction rates on the H_2O and CO_2 partial pressures were investigated in the range 10 to 95 kPa at temperatures between 715 to 920°C. The data were fitted to Langmuir-Hinshelwood expressions (section 4.2.3, paper I) according to the equations (2) and (3) below.

$$-(r_C)_{H_2O} = 0.25 e^{-8071/T} \cdot \frac{1.85 e^{-13303/T} P_{H_2O}}{1 + 1.85 e^{-13303/T} P_{H_2O}} \cdot C_C \quad (2)$$

$$-(r_C)_{CO_2} = 58 e^{-15733/T} \cdot \frac{0.035 e^{-7000/T} P_{CO_2}}{1 + 0.035 e^{-7000/T} P_{CO_2}} \cdot C_C \quad (3)$$

These equations represent an extension of the first order expression in equation (1), but do not take into account the retarding influence of H_2 and CO on the rate.

3.2. THERMOGRAVIMETRIC STUDY OF SHALE CHAR GASIFICATION

The conditions for gasification of shale char in gas mixtures of H_2O/N_2 , CO_2/N_2 , H_2O/H_2 , H_2O/CO , CO_2/H_2 and CO_2/CO have been investigated by thermogravimetry (paper III). It was shown (section 3.1.2, 3.1.3, paper III) that the reaction rate in the H_2O and CO_2 systems could be written as

$$-(r_C)_{H_2O} = k_1 \frac{k_2 P_{H_2O}}{1 + k_2 P_{H_2O} + k_3 P_{H_2} + k_3' P_{CO}^{0.25}} \cdot C_C \quad (4)$$

$$-(r_C)_{CO_2} = k_4 \frac{k_5 P_{CO_2}}{1 + k_5 P_{CO_2} + k_6 P_{CO}^{0.05} + k_6' P_{H_2}} \cdot C_C \quad (5)$$

The kinetic parameters of these equations are summarized in Table 4. As can be seen from the equations, the pressure dependence of carbon monoxide deviates strongly from the linear dependence predicted by the ordinary Langmuir-Hinshelwood expression. This effect was stated in both the steam and carbon dioxide systems and can be explained by the theory proposed by Hedden et al. (1959) (4). They suggest that similar to hydrogen, CO chemisorbes to the surface but additionally for CO, the carbon monoxide can act as an electron donator to the carbon surface. With increasing CO partial pressure this latter capability is considerably decreased due to saturation of the gitter with free electrons, and thus a non-linear partial pressure dependence will be observed. A very weak non-linearity was also found in the runs with CO₂/H₂ mixtures, giving an indirect indication of the occurrence of the shift reaction yielding carbon monoxide on the carbon surface. With the assumption that the H₂O and CO₂ gasification reactions occur in parallel, a total rate equation can be written according to equation (6).

$$-(r_C)_{\text{tot}} = \left[k_1 \frac{k_2 P_{\text{H}_2\text{O}}}{1+k_2 P_{\text{H}_2\text{O}}+k_3 P_{\text{H}_2}+k_3' P_{\text{CO}}^{0.25}} + k_4 \frac{k_5 P_{\text{H}_2\text{O}}}{1+k_5 P_{\text{CO}_2}+k_6 P_{\text{CO}}^{0.05}+k_6' P_{\text{H}_2}} \right] C_C \quad (6)$$

In runs with various partial pressures of H₂O, CO₂, H₂ and CO at different temperatures, the satisfactory validity of this equation was stated (Table 4, paper III). From the kinetic data on the H₂ and CO retardation it became clear that this effect is of particular importance. In Table 5 the influence of product retardation is shown by the ratio of the reaction rates with and without account for the H₂ and CO partial pressures. The calculations are done with constant H₂O and CO₂ partial pressures of 50 kPa and various H₂ and CO partial pressures. The conclusion follows that by overlooking the product retarding effect, a prediction of a large scale reactor performance will be far too optimistic.

Steam Gasification				
$-r_C = k_1 \cdot \frac{k_2 \cdot p_{H_2O}}{1 + k_2 \cdot p_{H_2O} + k_3 \cdot p_{H_2} + k_3' \cdot p_{CO}^{0.25}} \cdot c_C \quad (\text{mole C/kg char, s})$				
Constant	Preexponential factor (s ⁻¹)	Apparent Activation Energy (kJ/mole C)	Preexponential factor (Pa ⁻¹) ^α	Apparent Activation Energy (kJ/mole C)
k ₁	1.0 · 10 ¹⁶	404	-	-
k ₂	-	-	2.7 · 10 ⁻¹⁴	-188
k ₃	-	-	1.3 · 10 ⁻¹⁰	-144
k ₃ '	-	-	0.5	-10
Carbon Dioxide Gasification				
$-r_C = k_4 \cdot \frac{k_5 \cdot p_{CO_2}}{1 + k_5 \cdot p_{CO_2} + k_6 \cdot p_{CO}^{0.05} + k_6' \cdot p_{H_2}} \cdot c_C \quad (\text{mole C/kg char, s})$				
k ₄	9.6 · 10 ⁹	301	-	-
k ₅	-	-	3.4 · 10 ⁻⁸	-65
k ₆	-	-	1.1 · 10 ⁻⁴	-126
k ₆ '	-	-	9.4 · 10 ⁻⁸	-94

Table 4: Kinetic parameters for the steam and carbon dioxide gasification of Ranstad shale char.

H ₂ O gasification, P _{H₂O} = 50 kPa				CO ₂ gasification, P _{CO₂} = 50 kPa			
P _{H₂} P _{CO} (kPa)		850°C r _o /r _r	950°C r _o /r _r	P _{H₂} P _{CO} (kPa)		900°C r _o /r _r	975°C r _o /r _r
5	5	9.8	11.6	5	5	33.7	19.9
10	10	13.0	14.3	10	10	37.8	22.7
20	20	18.3	18.1	20	20	45.1	27.6

Table 5: Comparison of reaction rate, with and without account for H₂ and CO retardation, r_o = reaction rate without account for product retardation, r_r = reaction rate acc to eq. (4) and (5).

The influence on the reaction rate by impregnation of the char with alkali metal salts turned out to be small. The reactivity improvement obtained was a factor of 2 for impregnation loads of 0.1 to 1% by weight. (section 3.2 paper III). From a technical point of view, this enhancement of the reaction rate is not of a magnitude that it seems feasible. The increased process complexity involved can not be justified even if the potassium or calcium salts used could be derived from the shale ash and recycled.

3.3. GASIFICATION IN A CIRCULATING FLUIDIZED BED REACTOR

In most commercial scale gasification processes, the heat demand for the gasification reactor is supplied by combustion of part of the fuel with oxygen, produced for instance by air separation. The use of an air-blown reactor operating with segregated gas phases can be beneficial for investment and operating costs. In the reactor described in paper II, the heat generation is accomplished by combustion of part of the shale char with air, whereby the circulating char is simultaneously used as a carrier of physical enthalpy from the combustion to the gasification zone. In the reactor, no mixing of flue gas and raw product gas takes place. The solids circulation is maintained with pressure differences and without using moving parts such as valves and lock hoppers.

The reactor has been demonstrated to work with shale, and by using an inert heat carrier, it also has been operated on less ash rich fuels such as woodchips and peat (5). Due to the complex hydrodynamics of this reactor, no relevant kinetic information could be readily obtained. However, it was observed that the product gas composition and production was slightly different than expected from the data of the externally heated reactor (Figure 3a, b, paper II). The fraction of hydrocarbons is higher in the circulating fluidized bed. This is because the production of hydrogen and carbon oxides is lower than expected when using the kinetic data from the externally heated bed (Table 3, section 3.1.2 of summary).

A possible explanation could be that the char in the circulating bed is sequentially exposed to oxidizing and reducing atmospheres in the combustion and gasification zone. In the combustion zone it is likely that the oxygen preferably attacks the most reactive parts of the kerogen structure. Thus, when returning to the gasification zone the carbon concentration of the char particle has not changed considerably, but the char has a lower reactivity, since reactive parts of the kerogen have been burnt off.

An evaluation of the reaction rate using the same approach as for the steam tests in paper I, e.g. assuming the production of carbon oxides being a measure of the fixed carbon reaction rate together with perfect mixing of the solids in the reactor, a reactivity difference compared with the externally heated bed was obtained. At 800°C the reactivity of the char from the externally heated reactor was a factor 2.2 higher, which decreased to a factor 1.3 at 850°C. This tendency is expectable since with increasing temperature it is likely to assume the reactivity to be less influenced by easily activated and reactive structures.

In choosing between an oxygen and an airblown gasifier, the advantages of the latter such as the elimination of the oxygen manufacture has to be judged against disadvantages such as a more complex reactor design, a loss of gasification efficiency due to the heating up of the combustion air nitrogen and the need for two separate sulphur removal units. Comparisons of the circulating fluidized bed with an oxygen blown reactor are presented in section 4 of paper II.

3.4. A KINETIC STUDY OF THE HETEROGENEOUS SHIFT REACTION OVER SHALE CHAR AND KEROGEN FREE ASH.

The shift conversion is a central part in the reaction system of fixed carbon gasification. The ultimate gas composition is determined by the kinetic conditions for the reactions below.

The water gas reaction: $C(s) + H_2O(g) \rightleftharpoons CO(g) + H_2(g)$

The shift reaction: $CO(g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g)$

The Boudouard reaction: $C(s) + CO_2(g) \rightleftharpoons 2CO(g)$

From investigations on coal it is concluded in literature (6, 7) that the shift reaction occurs in series with the water gas reaction. Thus, no carbon dioxide is produced by direct reaction of carbon with steam according to the reaction:



It is further concluded that below 1000°C the shift reaction proceeds as a surface catalyzed heterogeneous gas/solid reaction.

Since no molar change of carbon takes place in the shift reaction, no information on steam decomposition rates can be obtained without knowledge of shift conversion kinetics.

The reaction rate of the shift reaction has been studied in a differential fixed bed reactor over shale char and carbon and sulphur free shale ash, (paper IV). The experimental data were fitted to power law equations describing initial rates in the temperature range between 650 and 800°C.

The forward reaction, defined as $CO + H_2O \rightarrow$ can be written:

$$-(r_{CO})_{char} = 7.3 \cdot 10^{-4} e^{-55500/RT} P_{H_2O}^{0.2} \cdot P_{CO}^{0.6} \text{ (mole/kg char,s)} \quad (7a)$$

and in analogy the reverse reaction:

$$-(r_{CO_2})_{char} = 6.7 \cdot 10^{-8} e^{-52000/RT} P_{H_2}^{0.8} \cdot P_{CO_2}^{1.0} \text{ (mole/kg char,s)} \quad (7b)$$

In the equations, the apparent activation energy is expressed in kJ/mole and the partial pressures in Pa.

The partial pressure exponents varied slightly in the temperature range and the data were evaluated with the arithmetic mean values inserted. The shift reaction was shown to be between one and two magnitudes faster than the fixed carbon reactions. The fastness of the shift reaction over carbonaceous surfaces has been concluded in a number of investigations (6, 8, 9, 10). With the assumption that the shift reaction is proceeding in series with the water gas reaction, the approach of equilibrium can be stated over shale char. Since the experiments have been carried out with binary gas mixtures, the equations are valid only with very low partial pressures of the products, e.g. far from equilibrium. By fitting the whole experimental material available at 800°C to a Langmuir-Hinshelwood type equation, a more generalized expression was obtained according to equation (8).

$$(r_{CO_2})_{char, 800^{\circ}C} = \frac{0.22 \cdot 10^{-10} (P_{H_2O} P_{CO}^{-1.25} P_{H_2} P_{CO_2})}{1 + 10^{-5} (1.4 P_{H_2O} + 0.05 P_{CO} + 0.05 P_{CO_2} + 1.6 P_{H_2})}$$

(mole/kg char, s) (8)

From this equation an equilibrium constant of 0.8 can be calculated, whereas the theoretical value is 1.02.

By combining equations 7a and b to a total rate expression

$$r_{tot} = r_{CO} - r_{CO_2} \quad (9)$$

a better approximation of the rate in the presence of both reactants and products can be expected. But from Table 2 of paper IV it comes clear that equation (9) is also favorably used far from equilibrium.

In analogy with the char runs, the kinetic over kerogen free shale ash have been thoroughly studied for the reverse reaction at 700 and 800°C. The forward reaction was studied only at 800°C. Below 650°C, the reaction rate could be neglected in both the char and the ash case.

The temperature dependence of the partial pressure exponents were found to be stronger for the ash than for the char. By using arithmetic means the rate is described by the following equation:

$$-(r_{\text{CO}_2})_{\text{ash}} = 2.6 \cdot 10^{-4} e^{-65300/RT} p_{\text{H}_2}^{0.44} \cdot p_{\text{CO}_2}^{0.44} \text{ (mole/kg, ash, s)} \quad (10)$$

Insertion of the values for the forward reaction yielded an experimental equilibrium constant of 3 at 800°C.

The reaction rate of char exceeds that of ash, and it is likely that the mechanisms for these two are quite different. The BET-areas differ greatly between char (15-25 m²/g) and ash (2m²/g). The iron oxide in the ash may contribute to the reactivity by alternation in valence number in a way that is similar to mechanisms proposed for commercial shift catalysis.

The fixed carbon gasification has been shown to be strongly retarded by CO and H₂. (paper III and section 3.2 of this summary.) The H₂ and CO molecules adsorbed are attached to the carbon surface as chemisorbed complexes, which might have an enhancing effect on the shift reaction rate.

In this fixed bed runs, some experimental remarks were stated. Compared with the fluidized bed, sintering occurred at considerably lower temperatures. No runs above 800°C could be successfully completed due to sintering. The residual char was very low in carbon and sulphur content and had ferromagnetic properties. A similar effect was found in the runs with ash. In the fluidized bed these agglomeration tendencies are of lesser importance due to the vigorous movement of the solids.

3.5. DISCUSSION OF THE KINETIC DATA

As described in sections 3.1, 3.2 and 3.4, kinetic parameters were obtained by different methods. For the fixed carbon gasification a continuously working fluidized bed and thermogravimetry were used, while the shift reaction was studied in a differential fixed bed reactor.

3.5.1. Comparison: Fluidized bed - Thermogravimetry

In the externally heated fluidized bed, the kinetic constants were evaluated from gas analysis and elementary analysis of discharged shale char. By this method, the gasification rate was determined by running the experiments on native shale. The gasification products e.g. CO and CO₂, were separated from the volatilization process by the gas analysis. From runs in nitrogen atmosphere, the contributions of carbon oxides originating from pyrolysis and limestone calcination were determined. The running conditions of the fluidized bed come closest to the situation in a real fluidized bed gasifier for several reasons. They are that the reactor operates in a continuous mode, at steady state, with the same particle sizes, and with similar particle heating rates as the large reactor. However, in other aspects the kinetic data obtained are limited in their validity. The runs conducted in pure H₂O and CO₂, reported in section 3.1.2 only describe the conditions of the first 0.5-0.6 m of bedheight in the large reactor. The runs carried out with nitrogen mixtures (section 3.1.3) show the dependence of the H₂O and CO₂ partial pressures on the reaction rate. Since the reaction products e.g. H₂ and CO strongly retard the reaction, as shown in section 3.2, these data are valid only for very low H₂ and CO partial pressures.

To obtain the full picture of gasification kinetics, experiments with high partial pressures of H₂ and CO had to be performed. For obvious reasons these runs were avoided in the fluidized bed, and preferably studied on a smaller scale. The method of thermogravimetry was found feasible, although some limitations were stated.

For two reasons, the runs must be carried out with prepyrolyzed char, where the volatilization should be more or less completed. Firstly, for the determination of the instantaneous carbon content, the initial conditions of the char must be known. Secondly, due to the small sample mass (10-15 mg), the off-gases could not be quantified, also implying the necessity for running the experiments with char, where the pyrolysis contribution can be neglected in the weight loss curve. Furthermore, the reactions of sulphur had to be accounted for. The kinetics of the FeS reactions with H_2O , CO_2 and H_2 were studied, and it was then assumed that the ironsulphides in the shale char reacted in the same manner as the model substance (section 3.1.1, paper III).

In figures 10 and 11 of paper III, it is shown that the reactivity of the char in the fluidized bed and thermobalance runs differ in the overlapping temperature interval. This difference could be related to the heating conditions during volatilization. The lower the heating rate and the lower the final pyrolysis temperature, the more reactive was the remaining char.

The char used in the thermobalance was heated at a rate of 0.5 K/s during pyrolysis, while the particle heating rate in the fluidized bed was calculated to the magnitude of 1000 K/s. Native shale devolatilized in the thermobalance at a rate of 20 K/s showed a reactivity in between that of the fluidized bed and the prepyrolyzed char.

Since the retarding effect of carbon monoxide and hydrogen was shown to be very strong, with a weak partial pressure dependence for carbon monoxide much of the difference in reactivity between the fluidized bed and TG tests can be explained by a retarding effect also for the fluidized bed runs, in spite of the low product gas partial pressures. As pointed out in section 3.3 of paper III, the experimental reactivity of the fluidized bed could be well described by using the TG kinetic parameters and the actual partial pressures in the bed of steam, carbon dioxide, carbon monoxide and hydrogen. Furthermore, it was pointed out in section 3.3 of this summary that the char gasified in the circulating fluidized bed and exposed to alternating reducing and oxidizing atmospheres showed a lower reactivity than char only exposed to steam. In this case the decreased reaction rate is possibly due to a burn-off of the most reactive parts of the kerogen structure in the combustion zone.

For the product gas retardation this could however, have a positive effect in that the carbon monoxide and hydrogen adsorbed is likely to be combusted in the oxidizing zone, yielding a refreshed carbon surface. The importance of this phenomena in oxygen blown fluidized beds has been pointed out by Squires (11). The definite influence of this cannot be judged for the shale case without knowledge about the relations between the particle mixing time in the reactor and the adsorption kinetics for carbon monoxide and hydrogen on the carbon surface.

Thus it can be concluded that the fixed carbon gasification rate is affected by factors other than temperature and partial pressures of reactants and products.

In summary, the gasification rate is chemically controlled over the whole temperature range investigated 650-950°C. No decrease in the apparent activation energy with increasing temperature was discovered. The char reactivity was influenced by the heating rate during volatilization. A higher heating rate gave a higher yield of volatiles, but also lower char reactivity. A lower reactivity, especially marked at temperatures below 850°C, was observed for shale char exposed to both oxidizing and reducing atmospheres in comparison with char reacted with steam only. The shift reaction proceeds at a rate considerably higher than the fixed carbon gasification, and could be assumed to approach equilibrium in connection with the water gas and Boudouard reactions.

In Table 6, the intervals of experimental validity are displayed for the kinetic constants obtained. The fluidized bed data should preferably be used at lower temperatures, up to 850°C, while the thermogravimetric data have their validity between 800 and 990°C. The retarding effects of H₂ and CO were measured in the high temperature range of 830 to 990°C. The shift reaction study was, due to sintering, limited to temperatures below 800°C.

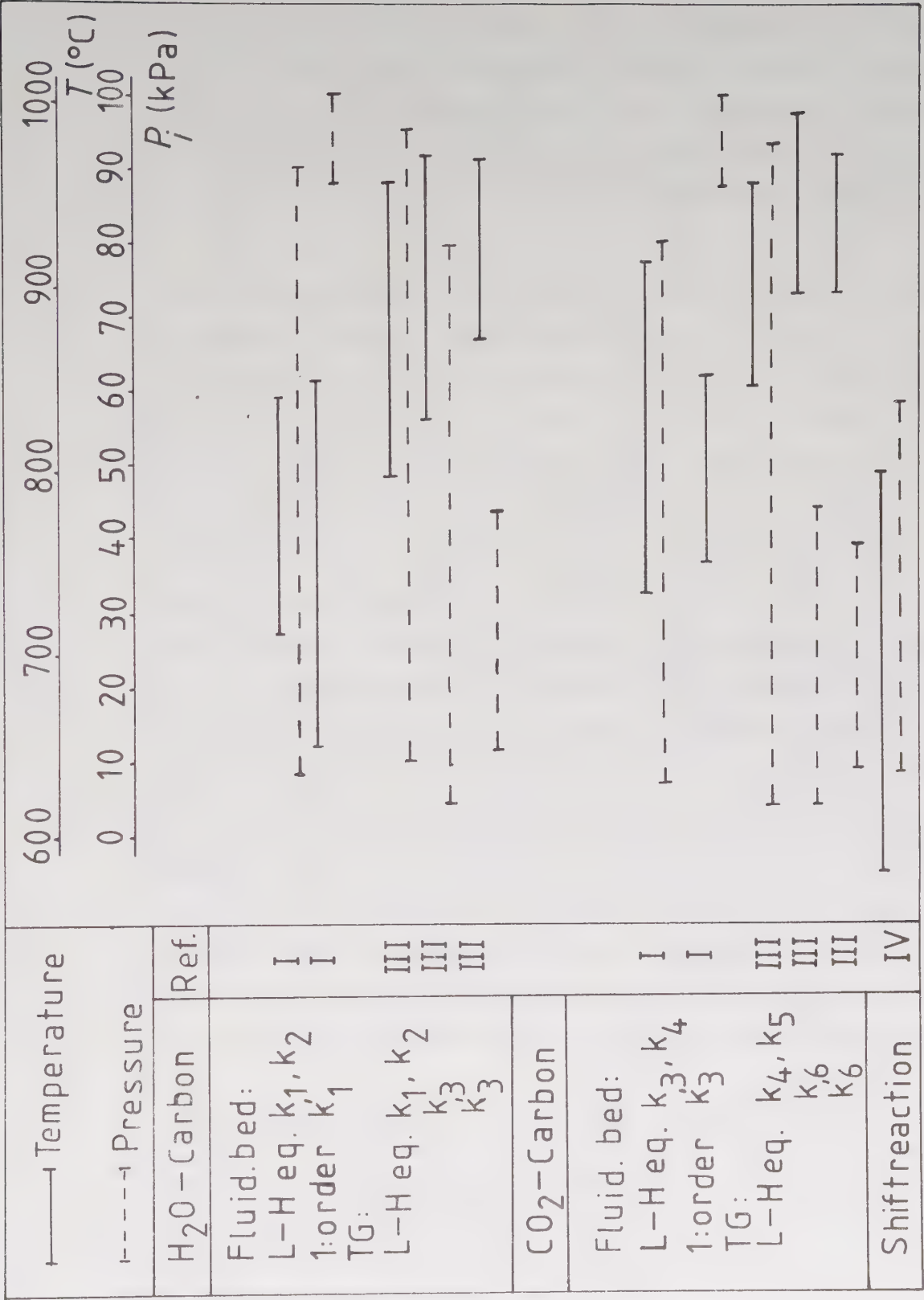


Table 6 :
Experimentally investigated ranges of temperature and pressure for the kinetic parameters.

3.5.2. Reactivity of shale compared with coal

Kinetic tests conducted under similar conditions allow comparison of the shale with other solid fuels. At Bergbauforschung GmbH in Essen, Federal Republic of Germany, a differential reactor system has been developed (12). In this reactor the reactivity of a number of coals, chars and lignites has been tested, and also the Ranstad shale.

In Figure 5, the reaction rate of Ranstad shale expressed as % C/min is compared with German coals and lignites from the Ruhr and Rhine area respectively (13). At 4 MPa the reactivity of the shale is in the order of that of coal and coal chars, but considerably lower than that of the lignite. A run at 200 kPa steam-pressure and the fluidized bed data at 100 kPa are also displayed in the figure. A clear pressure dependence for the reaction rate can be stated, which for coals turn towards a zero order dependence somewhere in the range 500 to 800 kPa, (16). Thus, from a kinetic point of view there are benefits to win in slightly elevated pressures, although in the case of synthesis gas production the methane yield is increased. On the other hand, for methanol synthesis, compression work can be saved in a pressurized gasification process. Furthermore, the performance of a gasifier is influenced by several factors, of which chemical kinetics is only one, although very important. During the planning of the research program for the shale gasification, the advantages of elevated pressures could not outweigh the foreseen technical difficulties for the large scale process, such as material problems due to the sulphur content, feeding and discharging of the very large solid streams, and a generally increased technical complexity due to an elevated pressure.

Since then it has become clear that most of the difficulties can be handled, and a gasification process operating at 500 kPa to 1 MPa can be considered as a feasible concept. An attempt to extrapolate the atmospheric pressure kinetic data to higher pressures (200 kPa and 4 MPa) failed to simulate the reactivities obtained in the Bergbauforschung runs. Using, in the temperature range 700 to 850°C the fluidized bed Langmuir-Hinshelwood expressions, the predicted reactivity at 200 kPa was about 2.7 times lower, and at 4 MPa a factor 7.5 lower than experimentally found in the Bergbauforschung tests.

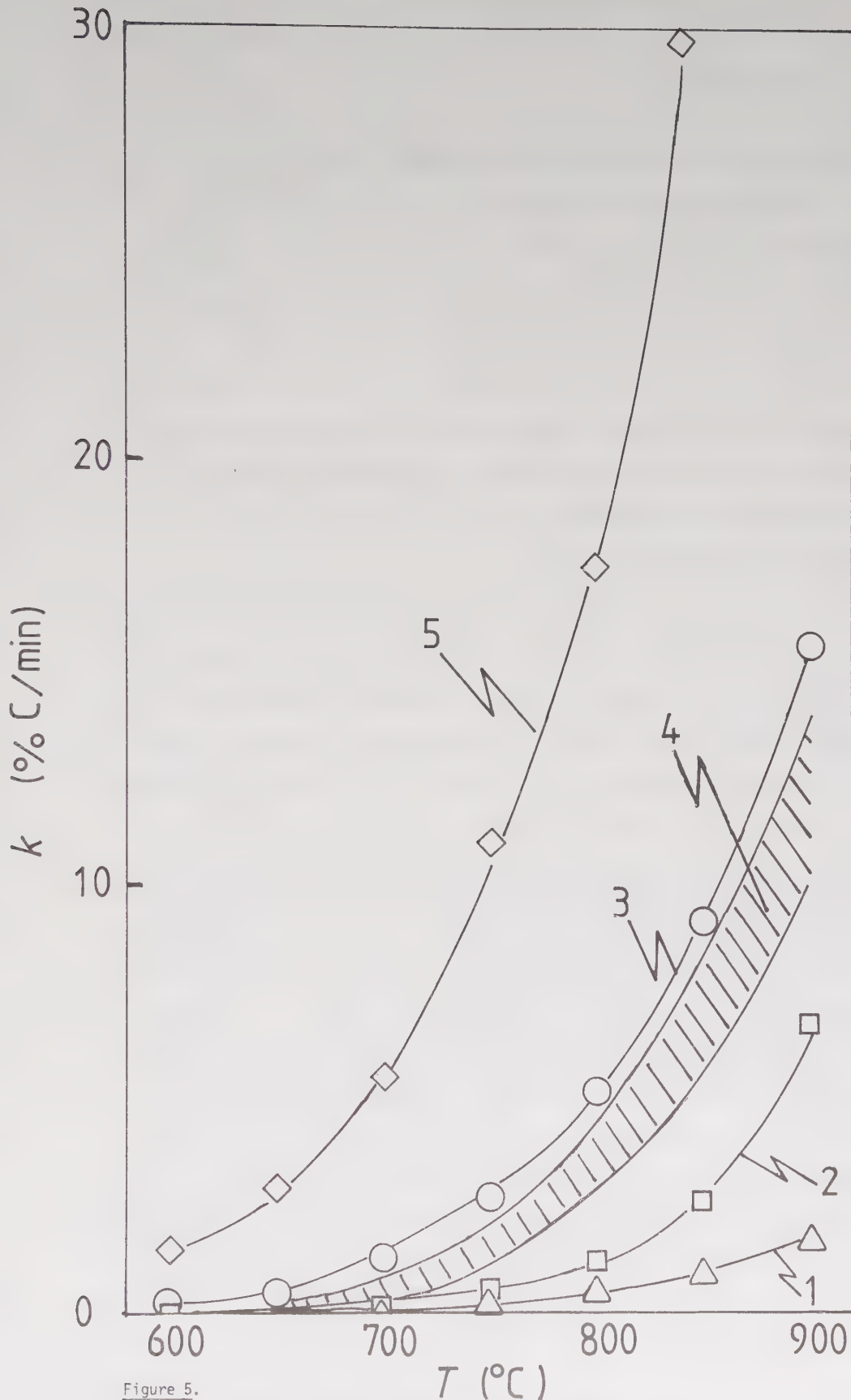


Figure 5.

Comparison of steam gasification rate for Ranstad shale and German coals and lignites. Data from Bergbauforschung GmbH, references (14), (15).

Code:

- 1: Ranstad shale, fluidized bed, $P = 100$ kPa.
- 2: Ranstad shale, $P = 200$ kPa.
- 3: Ranstad shale, $P = 4$ MPa
- 4: Different coals and chars from the Ruhr area, $P = 4$ MPa.
- 5: Lignite from the Rhine area, $P = 4$ MPa.

3.6. INFLUENCE OF KINETICS ON THE REACTOR SCALE-UP

3.6.1. Fluidized bed reactors

The performance of a gasifier operating under steady state conditions is given by the interchange between chemical reactions, mass transfer and hydrodynamics of the different phases within the reactor. As was pointed out earlier, the chemical step is rate controlling, and the relative slowness of the reactions imply a volume reaction throughout the whole bed of solids.

In fluidized beds, this is not always the case. For instance, the combustion reaction in a fluidized bed reactor is completed within some 10 centimeters above the gas distributor. Here the rest of bed only acts as a fuel reservoir and heat transfer medium. For the gasification reaction below 1000°C , the partial pressures of the reactants decrease only slowly with increasing bed height. Simultaneously there is an increase of the product gas partial pressures. In the fluidized bed, which has a gas phase residence time distribution somewhere between the extremes of complete mixing and plug flow, the degree of gas backmixing is an important parameter. As shown by the Langmuir-Hinshelwood equation, the gas backmixing influences the kinetics twofold. Firstly, backmixing lowers the reactant partial pressure at a given reactor level and secondly, the product gas retardation becomes more important. Since many laboratory and even small scale pilot plant experiments are only able to reproduce the lower sections of a large reactor, the demand for improved fluidized bed reactor models is essential. In recent years many proposals for fluidized bed reactor models have been developed, but none have shown the desired generality and simpleness for widespread practical use. In developing a reactor model for the shale gasification, a very simple gas dispersion model was chosen. This decision was made after a careful examination of different bubble and two-phase models which were available. In all cases it was concluded that no benefits could be achieved by using them, because the models were too complex or could only involve simple kinetics.

The algorithm developed with the gas dispersion model also allows for the assumption of plugflow on the gas phase. The solid phase is assumed to

be perfectly mixed, which is a good approximation, at least in comparison with the assumptions made for the gas phase.

As shown in paper V the influence of the axial dispersion has a quite limited influence on the gas production. The eddy diffusivity has been varied from zero to the rather unrealistic large value of $50 \text{ m}^2/\text{s}$, and the insensitivity of the gas production to the gas backmixing is explained by the kinetics of the fixed carbon gasification. The retardation effects by CO and H_2 are very strong, and for CO also quite insensitive to the CO partial pressure. This means that the retardation effects become important very early in the reactor, decreasing the negative influence of the backmixing very markedly. Thus, the simulations presented in paper V are therefore using the plug flow approximation for the gas phase, an approach which otherwise is to be used with care for fluidized beds. In the shale case this is however, a better approach than a more sophisticated model as pointed out by Park et al. (17). The shale particle sizes used and the high density of the char give a high minimum fluidizing velocity, differing only a factor 1.5 to 2 from the superficial fluidizing velocity. This fact creates a quite different hydrodynamic pattern in the bed compared with finer and less dense particles, as shown by Geldart (18).

The simulations conducted in V further show that high steam velocities are advantageous from a gasification efficiency point of view, in that the driving force for the gasification reactions is maintained at a higher level and that the product gas retardation is somewhat suppressed. To be noted is that this effect was obtained in spite of the higher energy demand necessary for heating up the additional steam.

The output from the reactor model has been compared with experimental data from the oxygen blown pilot plant gasifier operated by Ranstad skiffer AB at the Ranstad shale deposit. This reactor is 0.4 m in diameter, with a maximum effective bed height of 3.5 m. The reactor model could simulate the performance of the pilot reactor very well. A much less accuracy was obtained when assuming the combustion reactions

in the bottom consuming only fixed carbon. Both the carbon conversion and the gasification efficiency was over-estimated by the model. The approach of only gas combustion was found to fit the pilot data, as previously mentioned. This assumption probably comes much closer to reality, since the oxygen molecules will first meet the cloud of pyrolysis and gasification products surrounding each char particle.

3.6.2. Other types of reactors

Although the primary intention of the work has been to present kinetic information applicable to fluidized bed reactors, the validity of the data for other types of gasification reactors should be briefly outlined. Besides different types of fluidized beds, moving bed and entrained phase reactors can be utilized for gasifying the shale.

In using moving bed reactors, the kinetic data obtained are relevant. Since considerably larger particle sizes than those of the fluidized bed are used in this reactor (10-50 mm in diameter), the reaction rate can be reduced by intra-particle diffusion. Although a calculation of the efficiency factor for particles in the 10 to 50 mm range did not indicate any mass transfer influence, the kinetic data should be used with care in the higher temperature range, e.g. above 850°C. The conditions of volatilization are different from that of the fluidized bed, with a low heating rate in the drying and pyrolysis section of the bed. The composition of the pyrolysis products will change towards heavier hydrocarbons and an increased fraction of tar.

The entrained phase reactor generally operates in the high temperature range well above the melting point of the ash. For a shale application this would mean between 1400 and 1700°C. In contrary to other reactor types, here the residence time for the solids are in the same order as for the gas e.g. from a fraction of a second up to a few seconds. At these temperatures the conversion rate is entirely mass-transfer controlled. The external mass transfer resistance is minimized by using high gas velocities thus generating highly turbulent

conditions, and by using small particle diameters, ($< 100 \mu\text{m}$). For obvious reasons the kinetic data are not valid in these high temperature applications, where ultimately the gas composition is determined by the chemical equilibrium laws. The primary gasification products readily decompose in secondary reactions to hydrogen and carbon monoxide, with only traces of light hydrocarbons present in the product gas.

Considering the use of the moving bed and the entrained phase reactors a more comprehensive analysis must be carried out, taking into account, among other factors, the broad product spectra undesired in many process concepts for the moving bed reactor, and the loss of gasification efficiency in a high temperature process due to the low energy content of the shale.

4. FUTURE WORK

The present work has been aiming at an understanding of the fixed carbon gasification and has placed less emphasis on the fast pyrolysis and tar production steps. In an extension of the work, kinetic data on devolatilization and the conditions for tar formation and cracking will be areas of technical interest.

The reactions of sulphur are other subjects of great interest, which only have been overviewed in this work. The sulphur complex can preferably be studied both in terms of kinetics and as an engineering problem from the recovery point of view.

Since it has been pointed out in section 3.5.2 that the present data cannot be extrapolated to higher gasification pressures, a study of the reactivity at moderately elevated pressures, 0.5-3 MPa, is of great importance.

From a technical point of view, a more extensive study of the shift reaction in connection with the gasification is desired in finding the active agent of the product gas retardation in the steam and carbon dioxide systems. In connection with this, a study of the adsorption/desorption kinetics for the gasification products, H_2 and CO , together with reactivity tests in controlled alternating atmospheres is of interest for the reactor design.

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GASIFICATION OF SWEDISH BLACK SHALE IN THE
FLUIDIZED BED

Reactivity in steam and carbon dioxide atmosphere

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ABSTRACT

Uranium bearing black shale from the Swedish Ranstad deposit has been gasified in steam and carbon dioxide atmospheres in a bench scale fluidized bed over a temperature range of 650 to 920°C.

The investigation has demonstrated that the shale behaves chemically in much the same way as highly volatile coals. The gasification of fixed carbon showed reactivities comparable to coal chars, and the rate of gasification can be described by a Langmuir-Hinshelwood expression.

1. INTRODUCTION

Sweden holds extensive deposits of Cambrian alum shales with an organic carbon content. The total quantity is exceeding $50 \cdot 10^9$ tons, with the economically recoverable amounts around $5-6 \cdot 10^9$ tons, located in the provinces of Vaestergoetland and Oestergoetland.

The plans for exploiting the shale are primarily assigned to the uranium content of 200 - 300 g/ton, but also to the fossil energy in the kerogen and the occurrence of recoverable amounts of metals as K, Al, V, Mo and Ni.

2. DESCRIPTION OF THE RANSTAD SHALE

The shale utilized in this gasification study originates from the Ranstad area in Vaestergoetland. The uranium bearing shale seam in the Ranstad field has a thickness of about 8 m, with a slope of 3-4 m/1000 m. The shale amounts in the Ranstad deposit are estimated at $3 \cdot 10^9$ tons.

The inorganic part of the Ranstad shale, between 70 to 75% consists of silica and different illites and feldspars, quantities of some inorganic elements are given in Table 1. When mined, the shale contains large amounts of limestone, but the shale used in the gasification tests and in the uranium process has been cleaned to a residual limestone content of about 1.5 % by weight.

The fraction of the Ranstad shale, richest in uranium, which has been utilized in the gasification tests, has a kerogen content around 20 %. Proximate and ultimate analyses are given in the Tables 2 and 3. It can be seen from Table 3, that the sulphur content is high, with a total amount of 7 % by weight. The distribution is about 75 % pyritic, the rest being organic. The amount of sulphatic sulphur in freshly mined shale can be neglected.

According to Swanson (1960), it is known that kerogen can be separated into two different types, saprophelic, of animal origin, giving high oil yields, and humic kerogen, primarily derived from plants. Humic

kerogen has a much lower oil content and it is therefore likely that the kerogen in the Ranstad shale is of predominantly humic origin. The oil yield in a Fischer assay is very low, only about 1.5 wt-%.

On a moisture and ash free basis 44 % of the kerogen is volatile which is comparable to bituminous coals. Referring to Haslam and Russel (1927) the Boghead and Cannel coals are in some ways similar to shales with a very high fraction of volatile matter.

3. EXPERIMENTAL FACILITIES

The main purpose of this investigation has been to achieve a technical data base, from which the feasibility of gasifying Ranstad shale could be evaluated.

3.1 APPARATUS

The bench scale fluidized bed utilized for the tests is shown in Figure 1. The system is operated as a conventional bubbling bed at atmospheric pressure. The reactor is 10 cm in diameter, with an effective bed height of 65 cm. As an entrainment zone, with a height of 70 cm, the reactor is expanded to 20 cm in diameter above the bed surface. A sintered quartz plate is used as a gas distributor. The bed volume corresponds to a weight of 2.9 to 3.1 kg shale char at fluidizing conditions.

The reactor is heated to the desired reaction temperature by means of internal and external electrical coils. The temperature distribution in the bed is measured by 5 thermocouples placed on different bed levels, of which one is used as a transmitter to a PI temperature controller.

Entrained fines from the reactor are separated from the gas in two cyclones in series, and the fly ash is collected in sampling containers below the cyclones. The shale is fed to the reactor from a closed hopper, by a cooled screw feeder at a level 25 cm above the gas distributor. The feed rate can be varied in the order 0.5 to 10 kg/h by changing the cog wheels of the motor and screw axis.

A strictly measured flow of nitrogen is fed to the hopper, and is used both as a calibration flow in the gas analysis and as a diffusion bar to prevent steam condensation in the screw feeder. The char is discharged through an overflow at the bed surface into a tight container, from which sampling can be achieved. Incoming gases can be premixed, before passing an electrical heat exchanger, where preheating to about 400°C is possible.

Where necessary, hoppers and tubes are equipped with heating coils to prevent steam condensing. The whole apparatus is constructed from a low nickel stainless steel.

3.2 GAS AND SOLIDS ANALYSIS

Before leaving the equipment, a part of the gas is withdrawn for analysis. As mentioned earlier, nitrogen, or in some cases argon, are used as internal standards in quantifying the gas production. When introduced through the closed hopper into the fluidized bed, any later leakage is unimportant in the quantitative gas analysis.

The gas withdrawn will first pass a combined scrubber and condenser, where steam, tars and other heavy compounds are trapped. The water condensed is used as a scrubbing liquid. After the scrubber, the gas is further cooled in a tube and shell condenser, before entering filter and gas pump.

The incoming gas stream to the analysis equipment is divided between a gas chromatography system and an IR-analyzer. The GC system consists of two chromatographs equipped with TC detectors.

On the first chromatograph H_2 , O_2 , N_2 , CO and CH_4 are separated on a molecular sieve 5A column. For a delay of CO_2 , H_2S and C_2^+ hydrocarbons a Porapak N column is used which is back-flushed for venting. The second chromatograph utilizes a Porapak N column, where CH_4 , CO_2 , H_2S , COS and C_{2-3} hydrocarbons are detected. Carrier gas in the gaschromatographs is helium.

The outputs from the two GC:s are related by means of CH_4 , which is detected on both. Valve switchings, sampling intervals and integration are supervised and executed by two microprocessors.

The cycle time for an analysis is about 10 minutes. To monitor the immediate operating conditions, CH_4 is continuously recorded on the IR-analyzer.

Samples of shale, discharged char and fines from the cyclones are collected in nitrogen filled containers. Each sample is analyzed on calorific heating value and C, H, N and S content.

4. RESULTS

The tests have been performed in such a way that data concerning both physical properties and chemical kinetics could be obtained from the investigation.

4.1 FLUIDIZATION PROPERTIES

The minimum fluidization velocity has been measured in air at ambient conditions for different particle fractions and also for the particle distribution shown in Table 4. From the data an approximate correlation of the minimum fluidizing velocity to the particle diameter valid for the whole distribution can be obtained, according to equation (2).

The mean particle diameter in mm will be calculated according to Kunij-Levenspiel (1969)

$$\bar{d}_p = \frac{1}{\sum_i \left(\frac{x_i}{d_{p_i}} \right)} \quad x_i \text{ being the fraction of particles of size } d_{p_i} \quad (1)$$

$$u_{mf} = 0,43 \cdot \bar{d}_p^{0,85} \text{ (m/s)} \quad \{d_p\} \text{ mm} \quad (2)$$

Equation (2) is also valid for single particles below 1.5 mm, whereas for larger particle sizes the non-spherical shape of the char flakes becomes important and the equation will predict too high velocities.

The minimum fluidization velocity measured for the whole particle distribution in air at 20°C and at 800°C in steam gave values of 0.24 and 0.85 m/s respectively.

The superficial gas velocities used were of the order of 1 - 1.5 m/s, which is 1.5 to 2 times the minimum fluidizing velocity in the temperature range of interest. These velocities gave a good mixing of the bed, with no tendencies of segregation. The bed fluidizes in a strongly aggregative way and with a marked tendency to slugging, which can be explained by the flakiness of the char particles, and the ratio for bed height to diameter of 6. The char particles appear to possess good mechanical strength and the degree of attrition is low. The amounts of fly ash collected in the cyclones correspond to 2 - 3 % of the shale feed.

The bed can be operated without sintering or agglomeration of temperatures up to 950°C, which is 25 - 50°C below the ash melting point under reducing conditions.

4.2 STEAM AND CARBON DIOXIDE GASIFICATION

The reactivity of the shale has been studied at various bed temperatures, char residence times and inlet partial pressures of steam and carbon dioxide.

Although not normally used in terms of coal gasification, a mean residence time in case of the shale can be defined, because the volumetric flow of solids in and out of the reactor are of the same magnitude.

4.2.1 Rate controlling step

For the gasification of fixed carbon it is known from investigations by Wicke et al. (1956) that the chemical reaction is rate controlling at temperatures below 1000 - 1200°C. The high ash content of the shale could, however, introduce an internal mass transfer resistance, which could not be excluded a priori.

The influence of pore diffusion was investigated in two ways. Steam gasification tests at 800°C in a fixed bed differential reactor with one particle fraction between 1.4 - 2 mm and another with particle sizes below 0.1 mm prepared by crushing the coarse fraction gave only a 2 % difference in reaction rate. Secondly, char from the fluidized bed gasified in steam at 800°C and 1 h residence time was fractionated and analyzed with respect to carbon. No significant differences were found. The absence of pore diffusion can therefore be stated also for the gasification in CO₂-atmosphere, where the chemical reaction is even slower in the temperature interval investigated. The gasification reactions can therefore be kinetically described by ordinary volume reaction expressions.

4.2.2 Steady state gasification in steam atmosphere

The weight loss of shale when heated at a constant rate of 20 °C/min has been studied by thermogravimetric analysis in N₂, H₂O and CO₂ atmospheres.

The release of carbon compounds from the kerogen during nonisothermal heating can be roughly divided into three different steps. From Figure 2, a primary pyrolysis can be observed, beginning at 200°C with a maximum around 450 - 500°C. During this step the loosest bonds in the kerogen structure are broken, yielding carbon oxides, hydrogen, and hydrocarbons. Parallel to the carbonaceous decomposition, parts of the pyritic and organic sulphur are also volatilized.

Above 500°C, a much slower pyrolysis occurs, where the organic structure is rearranged towards a more and more graphitic structure, during which predominantly H₂ and CH₄ are given off. Furthermore it can be seen from Figure 2 that the gasification reactions of fixed carbon start to give an increased rate over nitrogen pyrolysis at 650 - 700°C in steam atmosphere and at 750 - 800°C in carbon dioxide.

In the fluidized bed, where the heating rate for a particle is extremely high, up to several thousands of °C per second, the condition of volatilization could differ from a slow heat up from both quantitative and qualitative points of view. It is known from several investigations,

Peters (1960), Peters and Bertling (1964) and Jones (1964) that rapid heating gives substantially more volatiles than slow heating rates.

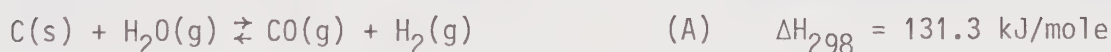
When gasified in steam atmosphere 1.1 ± 0.2 moles of carbon as C_1 to C_3 hydrocarbons per kg shale feed is volatilized. The production is almost independent of the bed temperature, with increasing char residence time a slight increase in production can however be observed. This corresponds to 1.1 to 1.5 wt-% of the shale or 7 to 10 % of the organic carbon. At higher temperatures a fairly slight shift in gas composition towards more CH_4 and less C_2 - C_3 hydrocarbons can be observed. A more extensive analysis of the degasification of the kerogen is beyond the scope of this investigation, and the bench scale reactor does not allow a complete control of the pyrolytic reactions, when tars and hydrocarbons higher than C_4 can not be detected in the analysis equipment.

In figure 3 the dry gas composition and the gas production is plotted against temperature at 1 h char residence time. The composition is affected to a rather small extent by the residence time. The fraction of hydrocarbons will decrease with both increasing residence time and temperature. At 0.5 h and $650^\circ C$ the C_{1-3} fraction of the gas is 27 %, while at 2 h and $850^\circ C$ it is only 5 %.

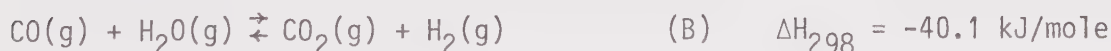
4.2.3 Reaction of fixed carbon with steam and carbondioxide

The reactions of solid carbon with steam and carbon dioxide can be summarized as:

Water gas reaction



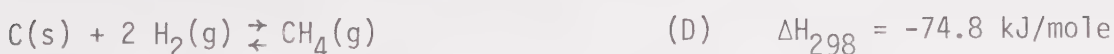
Shift reaction



Boudoard reaction



Methane formation



Reaction (D) is of minor technical importance at atmospheric pressure and can be neglected here.

The reaction mechanisms involved, kinetics of the steam-carbon and the carbon dioxide-carbon systems have been extensively investigated by a number of authors; Gadsby et al. (1946), Johnstone et al. (1952), Strickland-Constable (1947) and Wicke and Rossberg (1953). Generally it is assumed that there are a number of successive steps involved. In the reaction of steam with carbon it has been proposed that first the water vapour is adsorbed at an active site on the carbon surface. During the following reaction hydrogen is formed, while the oxygen will be fixed to the carbon in a complex. The release of the hydrogen formed is strongly influenced by the hydrogen absorption equilibrium. Then, the carbon-oxygen complex is split off as CO or further decomposed by reaction with another water molecule to form carbon dioxide and hydrogen. The variables determining the concentration of active sites are very complex, with interaction of properties of the coal such as crystallographic orientations, contents of hydrogen and sulphur, and metal constituents in the ash. The differences in reactivity between different carbonaceous structures can be explained with this approach by the concentration of active sites available.

In the Boudouard reaction (C), carbon dioxide is adsorbed at an active site, where an oxygenated carbon complex is generated during the liberation of one carbon monoxide molecule. The carbon complex can then decompose, giving carbon monoxide and a free active site. Similar to the steam-carbon reaction, the desorption rate of CO from the surface will reduce the rate of reaction.

In accordance with the mechanisms proposed, the reaction rates of fixed carbon, with steam and carbon dioxide have by several investigations (Gadsby et al. (1946), Johnstone et al. 1952) and Strickland-Constable (1947)) been shown to follow Langmuir-Hinshelwood expressions.

At low partial pressures of the reaction products e.g. hydrogen and carbon monoxide the retardation effects of these, due to adsorption equilibria, as previously mentioned, can be neglected.

The reaction rates in steam and carbon dioxide atmosphere could therefore be expressed according to the equations (3) and (4) respectively;

$$-(r_C)_{H_2O} = k_1 \frac{k_2 p_{H_2O}}{1 + k_2 p_{H_2O}} c_C \quad (3)$$

$$-(r_C)_{CO_2} = k_3 \frac{k_4 p_{CO_2}}{1 + k_4 p_{CO_2}} c_C \quad (4)$$

with c_C being moles of carbon per kg of char.

The constants k_1 to k_4 all follow an Arrhenius type equation

$$k_i = k_{i0} \cdot e^{-E_i/RT} \quad (5)$$

Under conditions with very low steam and carbon dioxide conversions at atmospheric pressure the expressions (3) and (4) can be simplified to pseudo first order kinetics where the contributions of steam and carbon dioxide can be included in the rate constants according to the equations (6) and (7).

$$-(r_C)_{H_2O} = k_1' \cdot c_C \quad (6)$$

$$-(r_C)_{CO_2} = k_3' \cdot c_C \quad (7)$$

4.2.4 Experimental

The kinetic parameters in the equations (3), (4), (6) and (7) have been determined for the gasification in steam and carbon dioxide at low partial pressures of product gases.

To evaluate the constants the inlet pressures of steam and carbon dioxide have been varied by dilution with nitrogen in the range 0 - 100 kPa, at 100 kPa total pressure.

The effect of physically adsorbed nitrogen on the carbonaceous surface can be neglected at the gasification temperatures according to investigations of Hasz and Barrere (1969).

In a steam-nitrogen atmosphere, the tests have been conducted with temperatures 650 to 850°C, and 1 hour char residence time. For runs in pure steam, the residence time have also been varied from 0.5 to 2 hours.

The carbon dioxide runs have all been accomplished at 1 h char residence time in the temperature range 750 to 920°C.

4.2.5 Steam atmosphere

The reaction rate of fixed carbon can be related to the production of CO and CO₂ according to the reactions (A) and (B). Carbon oxides will also be produced during volatile matter pyrolysis and by decomposition of inorganic carbonates in the ash. By runs in N₂ these contributions have shown to be quite small. They have therefore not been accounted for and the reaction rate is given by equation (8).

$$(r_C)_{H_2O} = (M_{CO,CO_2})_{\text{detected in gas}} \quad (\text{moles C/kg char,s}) \quad (8)$$

The running conditions, temperature, steam partial pressure and reaction rates calculated from equation (8) are summarized in Table 5 for the runs with steam-nitrogen mixtures. The tests with various steam partial pressures have been evaluated numerically by mean of a weighted least square regression with the objective function;

$$Q = \sum_{i=1}^n \left(\frac{(Y_C)_i - (Y_m)_i}{(Y_m)_i} \right) \quad (9)$$

Y_C = calculated reaction rate r_C/C_C according to equation (3)

Y_m = measured reaction rate r_C/C_C .

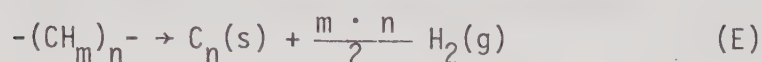
The correlation between the observed reaction rates and equation (3) is shown in Figure 4. The frequency factors and the apparent activation energies determined are given in Table 6.

In Figure 5, showing the Arrhenius plot for the pseudo first order equation (6), the regression has been made on data from gasification at three char residence times, 0.5, 1 and 2 hours. The kinetic constants obtained were $k'_{10} = 1000 \text{ s}^{-1}$, $E'_1 = 147 \text{ kJ/mole}$.

4.2.6 Carbon dioxide atmosphere

For the Boudouard reaction (C) the rate of gasification can be related to the carbon monoxide production. The amount of CO detected must in this case be corrected by the contribution of CO produced by the reverse shift reaction (B).

As mentioned earlier, hydrogen is produced through the decomposition of the kerogen structure, with the assumed reaction



This pyrolytic hydrogen production has been correlated to a first order equation with respect to hydrogen content in the char, C_H , from gasification tests in steam atmosphere.

$$-(r_H) = k_5 C_H \quad (10)$$

The decomposition rate is defined as the difference between the total hydrogen production and theoretical hydrogen production related to the actual carbon monoxide and carbon dioxide production according to the water/gas (A) and shift reaction (B). From the Arrhenius plot in Figure 6, the kinetic parameters were estimated at

$$k_{05} = 37 \text{ s}^{-1} \text{ and } E_5 = 96 \text{ kJ/mole}$$

With the assumption that this hydrogen production occurs independently of gas atmosphere, it is reasonable to assume that the hydrogen reacts with CO_2 according to the reverse shift reaction (B), due to the large CO_2 excess in the reactor (Bjerle et al. 1979). The production originating from the Boudouard reaction could therefore be written

$$(r_C)_{CO_2} = \frac{1}{2} \left[M_{CO \text{ detected}} - \frac{1}{2} (r_H) + M_{H_2 \text{ detected}} \right] \text{ (moles C/kg char, s)} \quad (11)$$

The experiments for determination of the constants in the equations (4) and (7) have been conducted in the same way as for the steam case in the temperature range 750 - 920°C. Table 5 gives the experimental conditions for the CO_2 - N_2 runs, the kinetic parameters in equation (4) are summarized in Table 6, and the correlation between observed and calculated reaction rates are shown in Figure 7.

By analogy with the steam case the kinetic constants in equation (7) have been evaluated for the gasification in pure CO_2 . From the Arrhenius plot in Figure 8 the constants $k'_{30} = 8\,780\text{ s}^{-1}$ and $E'_3 = 171\text{ kJ/mole}$ were obtained.

4.2.7 BET area

The reactivity of a char is very complicated to define. As mentioned earlier it can be related to the concentration of active sites in a complex manner, of which the specific surface could be a measure. The B.E.T. area of a sample is not equivalent to the true area, but will indicate relative changes.

In Figure 9 the BET area has been plotted against the carbon content of steam gasified chars. As can be seen both the shale and the carbon free ash have low and quite similar areas of $2\text{--}3\text{ m}^2/\text{g}$. During pyrolysis, the structure is broken up, and areas up to $30\text{ m}^2/\text{g}$ are created. Campbell (1978) has investigated pyrolysis of bituminous coals and found a very strong increase in the BET area during pyrolysis.

With decreasing carbon content the area decreases lineary down to that of carbon-free ash.

5. DISCUSSION

5.1 COMPARISON SHALE - COAL

From the data on the fundamental properties of the shale the relationship to highly volatile coals were stated. On the other hand, the extreme ash content introduces differences, as the shale in contrast to coals does not undergo any volumetric changes during thermal treatment.

When gasified, the carbon concentration of the char and the gas production can therefore be related to a defined bed mass, and a mean residence time for the char can be determined.

Investigations of the kinetics of shale char are rarely reported in literature, most work has naturally been carried out on coal chars. First

order kinetic parameters on coal char gasification in steam and carbon dioxide atmosphere have been given by Pulsifier et al. (1976), and Dutta et al. (1977) respectively. When compared with their data the shale char has a lower reactivity. Generally the shale char has somewhat lower energy of activation and corresponding lower pre-exponential factors, than the coal chars. This could be an indication of a mass transfer influence in the shale kinetics, but this is, on the other hand, contradicted by the tests on rate controlling step under section 4.2.1. When comparing the different data one should also bear in mind the in many cases different experimental conditions.

The kinetic data obtained in equation (3) show agreement with data from Wanzl et al. (1978), where reactivities of lignite and bituminous coal chars have been fitted to a Langmuir-Hinshelwood expression.

Burnham (1979) investigated the reactivity of fixed carbon in CO_2 -atmosphere for Colorado oil shale. When compared to the Ranstad shale he found higher activation energies and pre-exponential factors, 205 - 234 kJ/mole and $0.53 - 10.2 \cdot 10^8 \text{ s}^{-1}$ compared with the Ranstad shale of 171 kJ/mole and $8.8 \cdot 10^3 \text{ s}^{-1}$ respectively.

In equation (11) utilized for the calculation of the reaction rate in CO_2 -atmosphere, the contribution of the correction terms are quite big at lower temperatures, which creates an uncertainty in the data. On the other hand, the corrections are based on experimental findings, and the expression is an attempt to isolate the Boudouard reaction and will give a more true picture of the char gasification rate than an uncorrected expression, based on the total CO production only.

5.2 INFLUENCE OF THE FLUIDIZED BED

Normally a fluidized bed is not well suited for accomplishing kinetic investigations, due to its complex hydrodynamic pattern, making it very difficult to separate the kinetic information from a mass transfer and/or hydrodynamic influence.

A fluidized bed influences kinetic data primarily in two ways. First, the backmixing of the gas phase, with deviation from plugflow introduce

an uncertainty about the partial pressures of the gas components at different points of the bed. Secondly the gas in the bubble phase could be in poor contact with the solids, and for very fast chemical reactions, a mass transfer resistance can occur between the bubble and emulsion phases in the bed.

In applications such as the shale gasification with the laboratory scale fluidized bed, the complications mentioned can be shown to be of very little, if any, importance.

Due to the shallowness of the bed and the very low conversion of the gaseous reactants, in most cases below 10 %, the bed can be looked upon almost as a differential reactor, and the influence of gas back mixing will be negligible. Secondly, with the particle sizes used in the experiments, the minimum fluidization velocity differ from the actual velocities only by a factor 1.5 to 2. This means that a considerable amount of the gas flow will pass the emulsion phase.

Geldart (1973) has shown in his classification of solids according to their fluidizing properties, that coarse particles ($d_p > 0.5 \text{ mm}$) in contrast to fine powders are unable to "imbibe" gas in the emulsion phase, due to the absence of a laminar film around the particle. The surface of the coarse particle will therefore be exposed to gas phase more or less similar to the bubble gas composition. A bed of coarse solids will therefore show a good gas-solid contact, and mass transfer and kinetics will not depend on local conditions around the particle.

The absence of a mass transfer resistance due to diffusion of steam and carbon dioxide from the bubble phase to the particles is also likely to be negligible as the bubble growth is limited and at the temperatures of interest the gasification reactions are slow compared to the molecular diffusion.

6. CONCLUSIONS

The work described here has shown that Swedish black shale can be gasified by steam and carbon dioxide in a fluidized bed. The chemical reaction has shown to be rate controlling with particle sizes and temperatures used. The shale kerogen has characteristics, more comparable to highly volatile coals than to oil shales.

When gasified in pure steam atmosphere a medium BTU gas is produced. The gas composition and production have shown to be affected by not only the temperature but also the char residence time. At the shortest residence time, 0.5 h, the gas has a predominately pyrolytic origin and it appears that the gasification of fixed carbon will not become of importance as long as there is a volumetric flow of pyrolysis products from the kerogen structure.

The apparent kinetic parameters, determined by fitting the reaction rate in nitrogen/steam and nitrogen/carbon dioxide mixtures as well as pure steam and carbon dioxide, to Langmuir-Hinshelwood and pseudo first order kinetic expressions have indicated char reactivities in the same order as those of bituminous coal chars.

ACKNOWLEDGEMENTS

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TABLE 1

Ranstad Shale, Inorganic Constituents

Element	Weight %
SiO ₂	45.0
Al	6.6
Fe	6.0
K	4.0
Mg	0.50
Ti	0.35
U	0.030
V	0.075
Mo	0.034
Cr	0.032
Ni	0.020
Rare earth metals	0.04

TABLE 2

Ranstad shale, proximate analysis, wt-%

Moisture (as recieved)	5.0
Volatile matter (moisture free, MF)	13.0
Fixed carbon, MF	12.1
Ash, MF	74.9

TABLE 3

Ranstad shale, ultimate analysis

	kerogen	raw shale, MF
% C	73.7	15.0
% H	6.9	1.4
% O	~ 8.5	~ 1.7
% N	1.9	0.4
% S	9.0	7.0 { 5.2 inorg 1.8 org
Cal. heat of com- bustion (MJ/kg)	27.0	6.6

Molar formula, kerogen

C₁₀₀ H₁₁₂ O₉ N₂ S₅

TABLE 4

Sieve analysis (wet method, wt-%)

D_p (mm)	Shale	Char $\bar{\theta} = 1$ h, $T = 800^{\circ}\text{C}$
> 2	0.5	1.8
2 - 1	47.2	49.3
1 - 0.8	5.2	6.1
0.8 - 0.63	12.2	12.8
0.63 - 0.4	14.2	14.0
0.4 - 0.2	10.3	10.2
0.2 - 0.1	5.3	4.1
0.1 - 0.05	1.9	0.7
< 0.05	3.1	0.7

TABLE 5

Ranstad shale, steam gasificationTotal pressure: 100 kPa, Dilution gas: N₂

T (°C)	P _{H₂O} (kPa)	r _C /C _C (s ⁻¹)
715	48	1,50 · 10 ⁻⁵
720	96	1,92 · 10 ⁻⁵
723	28	0,42 · 10 ⁻⁵
730	11	0,25 · 10 ⁻⁵
740	94	2,44 · 10 ⁻⁵
755	50	2,33 · 10 ⁻⁵
760	10	0,58 · 10 ⁻⁵
783	28	1,47 · 10 ⁻⁵
785	47	2,50 · 10 ⁻⁵
788	94	4,78 · 10 ⁻⁵
790	8	1,61 · 10 ⁻⁵
840	9	2,28 · 10 ⁻⁵
840	22	4,06 · 10 ⁻⁵
840	43	5,11 · 10 ⁻⁵
840	90	9,89 · 10 ⁻⁵

Carbon dioxide gasificationTotal pressure: 100 kPa, Dilution gas; N₂

T (°C)	P _{CO₂} (kPa)	r _C /C _C (s ⁻¹)
770	18	0,78 · 10 ⁻⁵
770	42	0,98 · 10 ⁻⁵
775	8	0,53 · 10 ⁻⁵
825	33	1,81 · 10 ⁻⁵
825	79	4,08 · 10 ⁻⁵
873	82	8,81 · 10 ⁻⁵
875	36	4,19 · 10 ⁻⁵
910	8	4,19 · 10 ⁻⁵
920	18	6,64 · 10 ⁻⁵

TABLE 6

Kinetic constants in the equations (3) and (4).

$$r_c = -A_0 e^{-E_1/RT} \cdot C_c \frac{B_0 e^{-E_2/RT} \cdot P_i}{1 + B_0 e^{-E_2/RT} \cdot P_i} \qquad i = \text{H}_2\text{O}, \text{CO}_2$$

	Preexponential factor A_0 (s^{-1})	Activation energy E_1 (kJ/mole)	Preexponential factor B_0 (Pa^{-1})	Activation energy E_2 (kJ/mole)
H ₂ O, Eq (3) k_1 k_2	0.25	67.1	-	-
	-	-	1.85	110.6
CO ₂ , Eq (4) k_3 k_4	58	130.8	-	-
	-	-	0.035	58.2

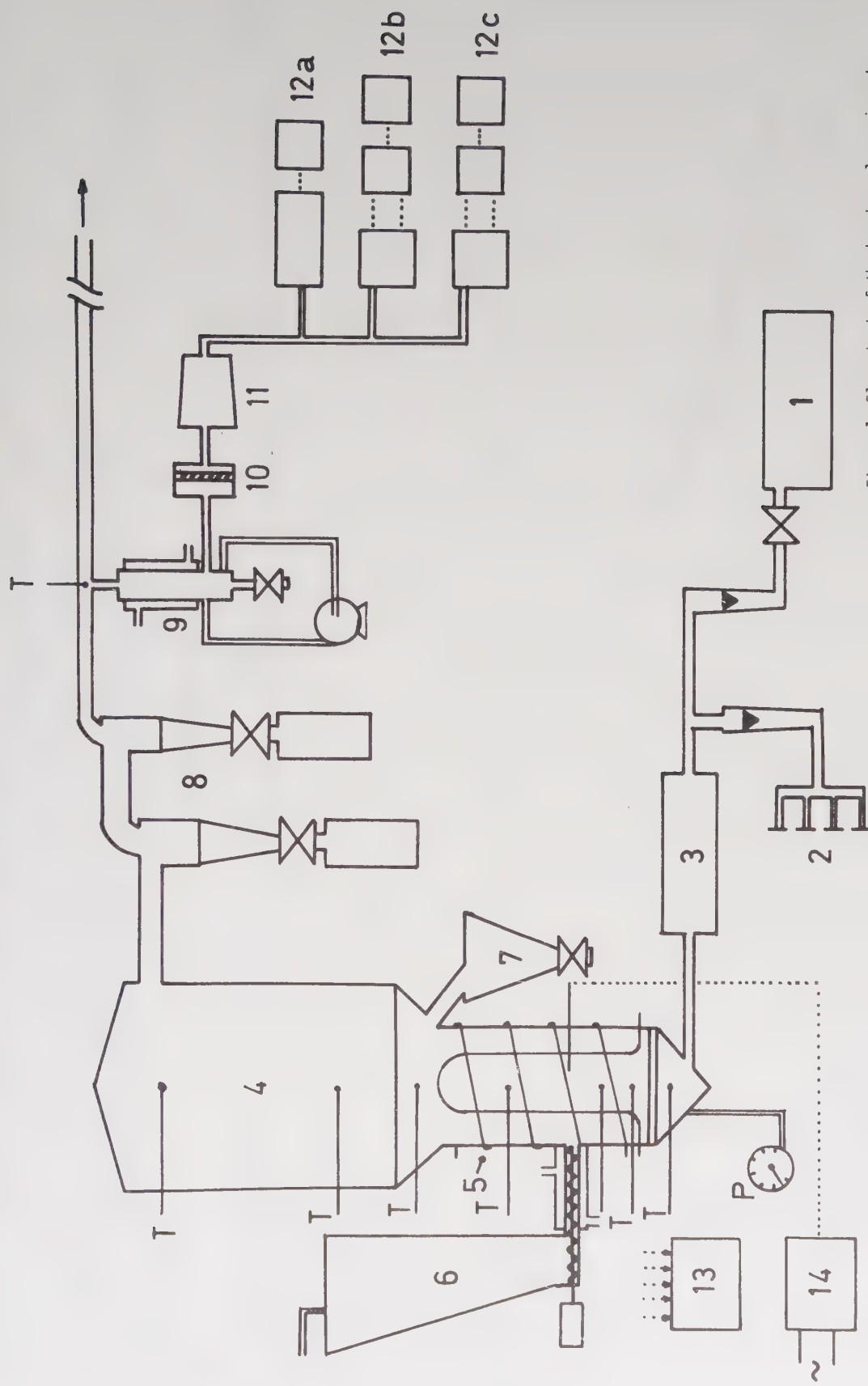


Figure 1. Flow sheet of the bench scale equipment

- | | |
|--------------------------------|---|
| 1. Steam generator | 9. Condenser, tar scrubber |
| 2. Inlet, noncondensable gases | 10. Filter |
| 3. Gas preheater | 11. Gas pump |
| 4. Fluidized bed reactor | 12a, IR gas analyzer |
| 5. Heating coils | 12b,c. Gas chromatographs and microprocessors |
| 6. Shale storage | 13. Temperature recorder |
| 7. Char hopper | 14. Temperature controller |

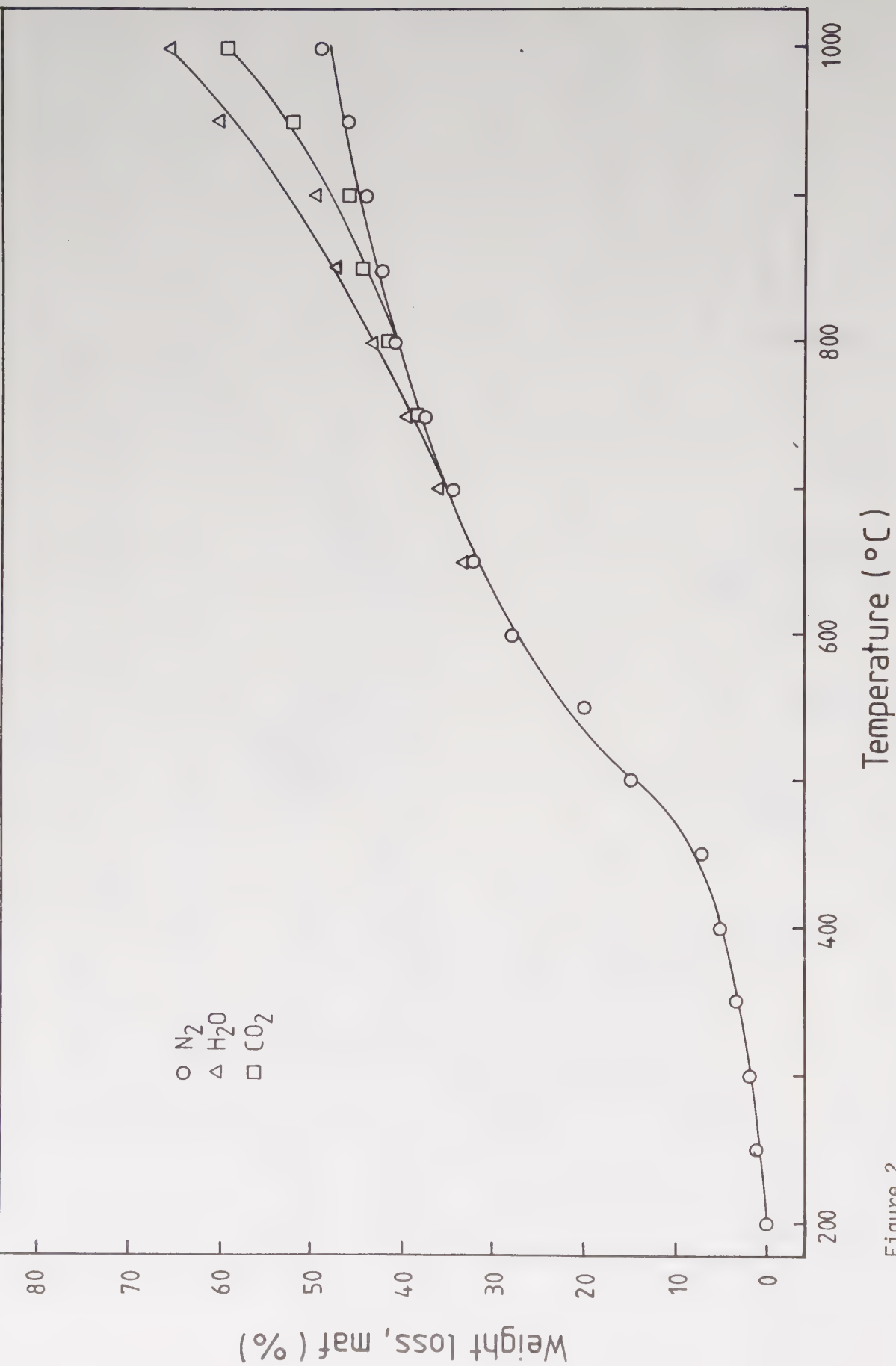


Figure 2

Ranstad shale. Nonisothermal heating. Thermobalance, N_2 , CO_2 and H_2O atmosphere. Heat rate $20^\circ C/min$. Weight loss (moisture and ash free basis).

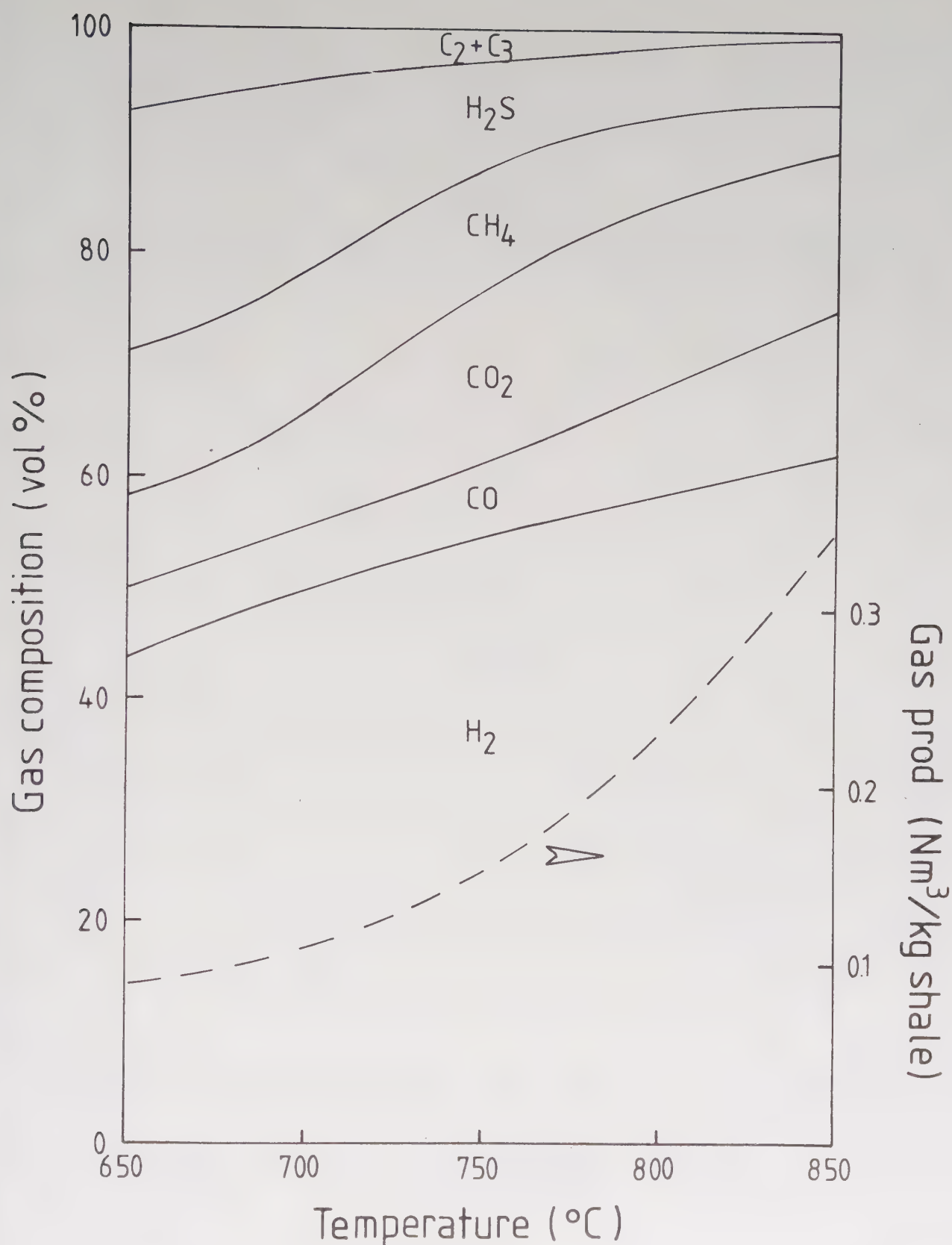


Figure 3

Ranstad shale. Steam gasification. Char residence time: 1 h.
 Gas composition (vol-%) and corresponding gas production
 (Nm³/kg shale).

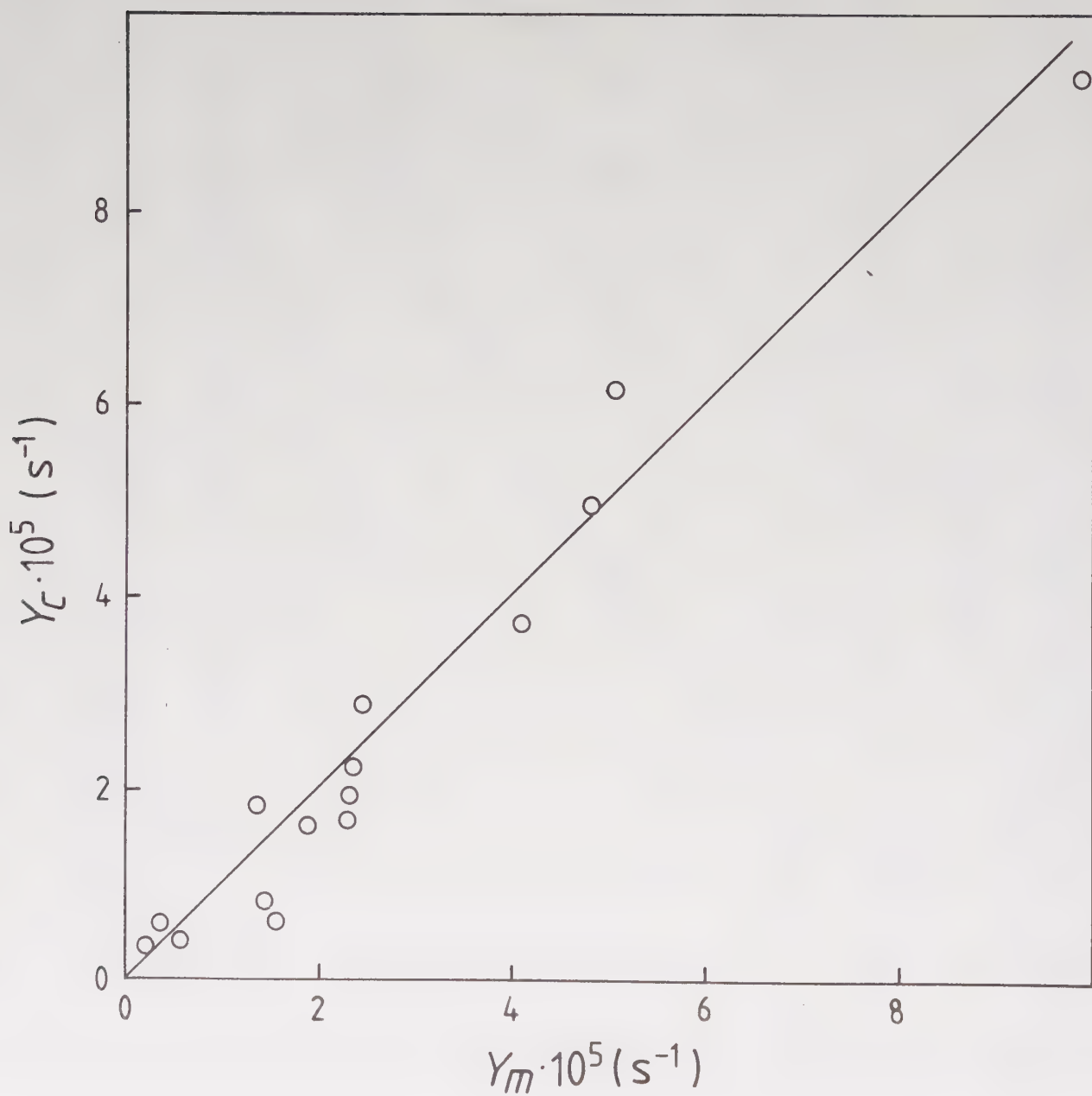


Figure 4

Ranstad shale. Steam gasification. Correlation of equation (3).

Y_c = Calculated reaction rate, Y_m = Measured reaction rate.

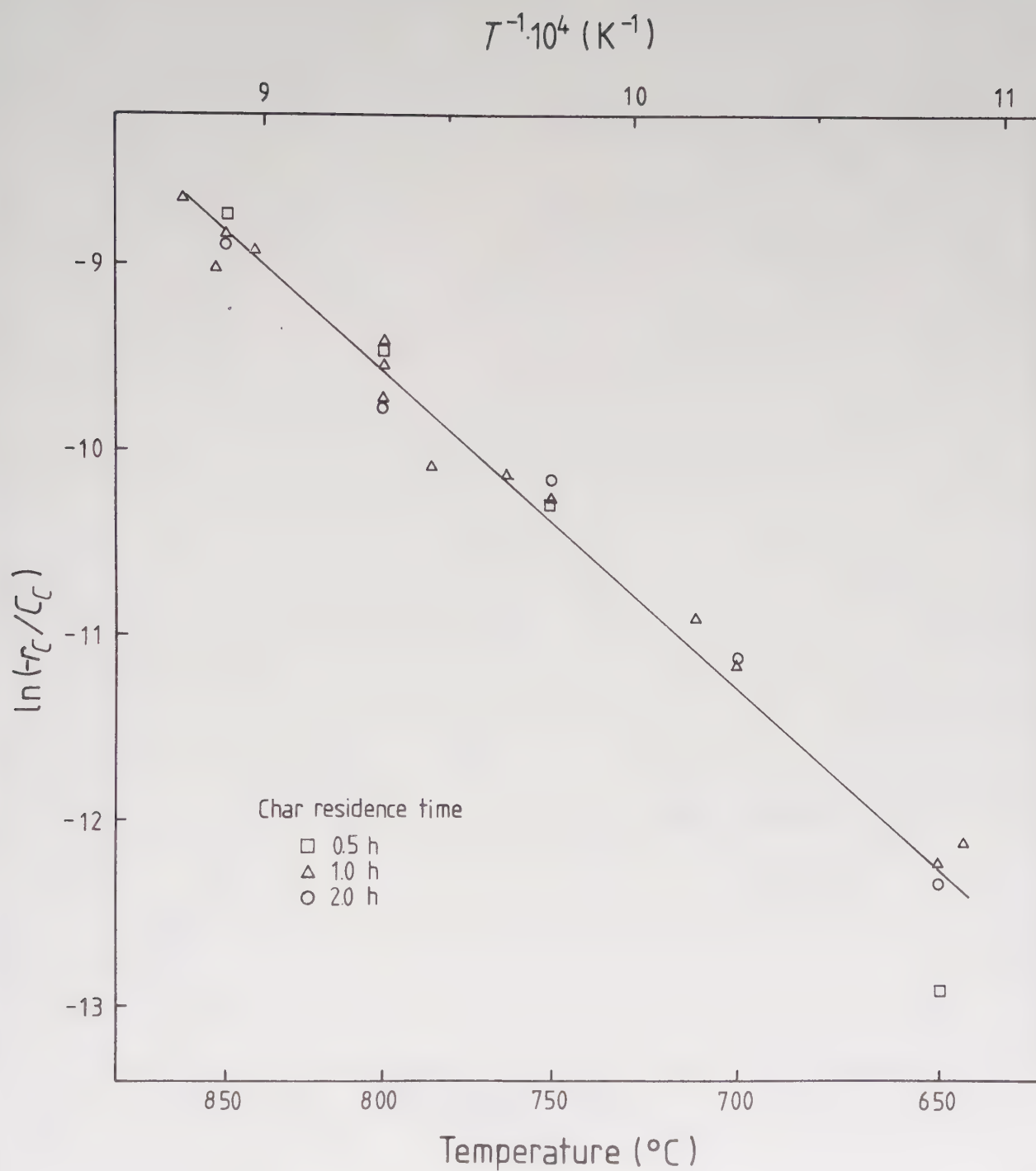


Figure 5

Ranstad shale. Steam gasification.

Arrhenius plot. $P_{\text{H}_2\text{O}} = 100 \text{ kPa}$. Time base: Seconds.

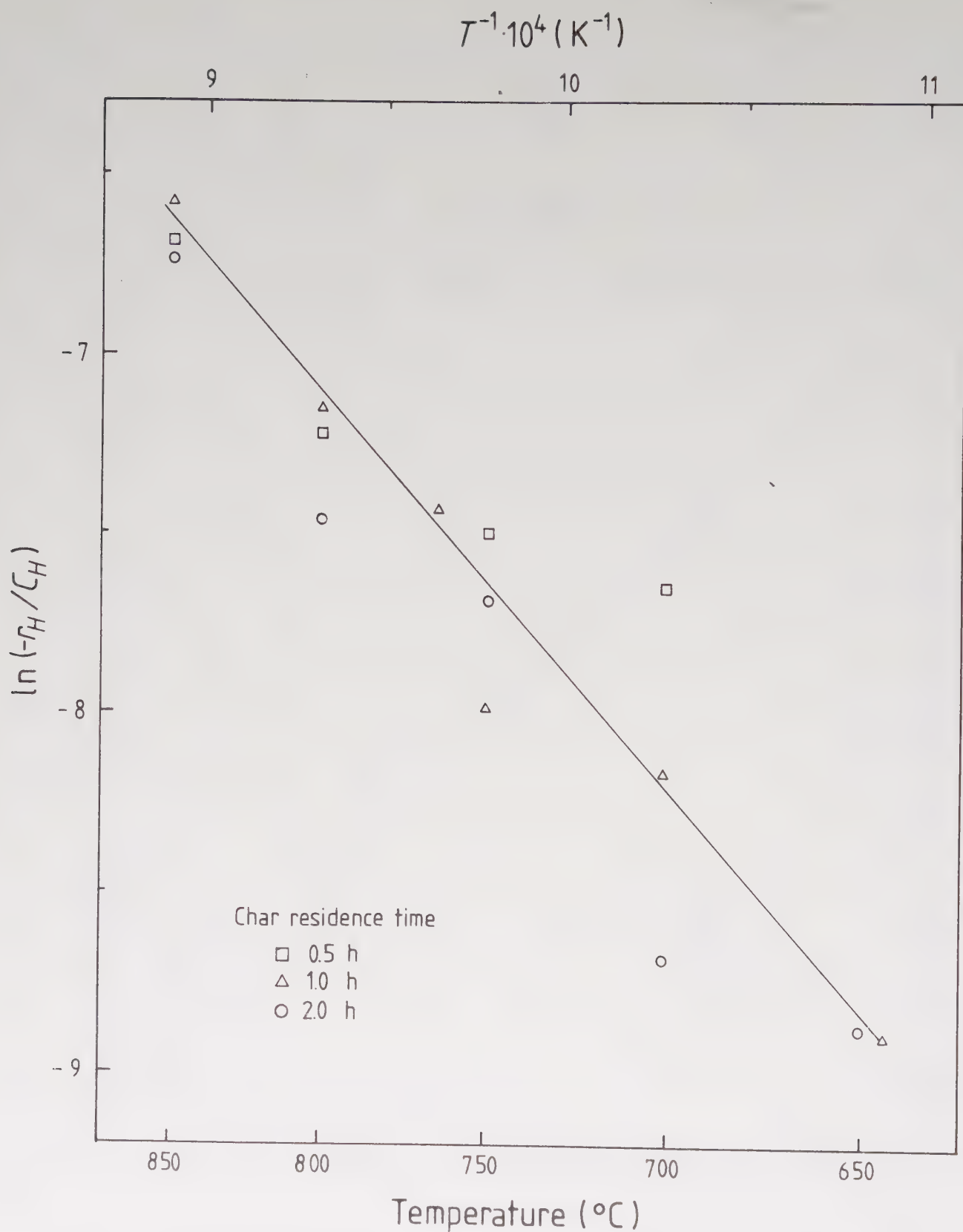


Figure 6

Ranstad shale. Steam gasification. $P_{H_2O} = 100$ kPa.

Arrhenius plot. Hydrogen production by kerogen decomposition.

Time base: Seconds.

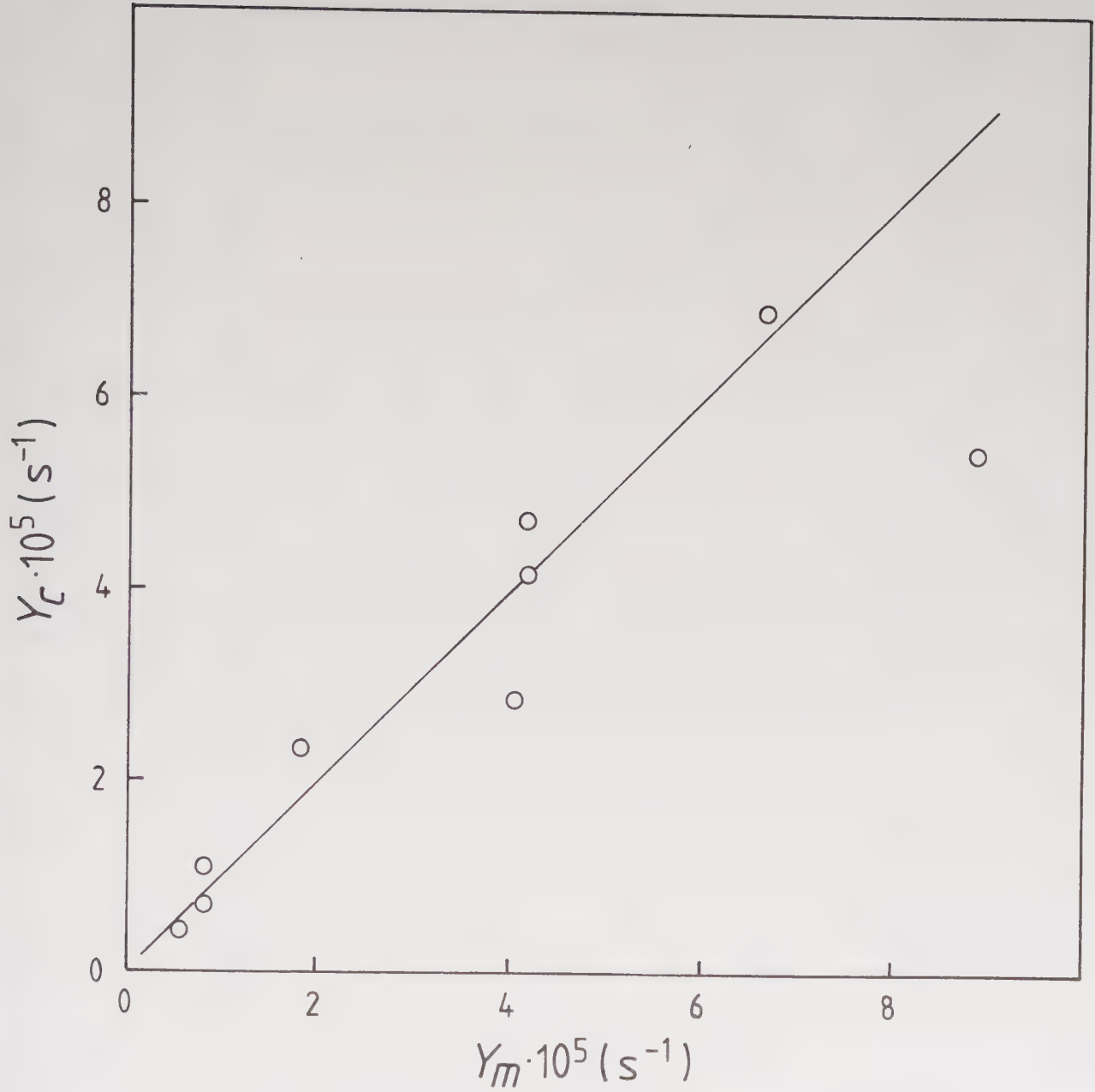


Figure 7

Ranstad shale. Carbon dioxide gasification.

Correlation of equation (4).

Y_c = Calculated reaction rate, Y_m = Measured reaction rate.

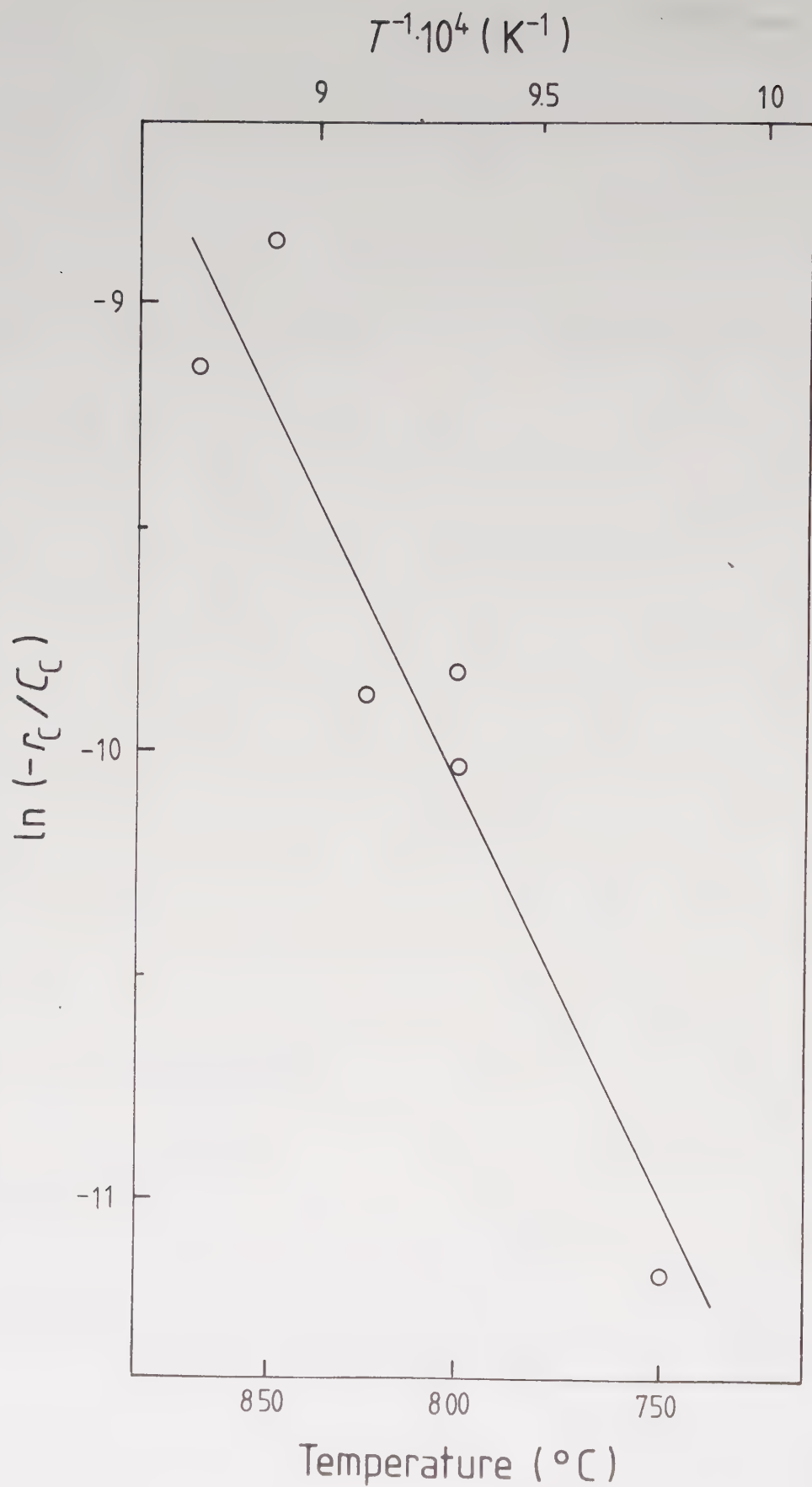


Figure 8

Ranstad shale. Carbon dioxide gasification.

Arrhenius plot. $P_{\text{CO}_2} = 100 \text{ kPa}$.

Time base: Seconds

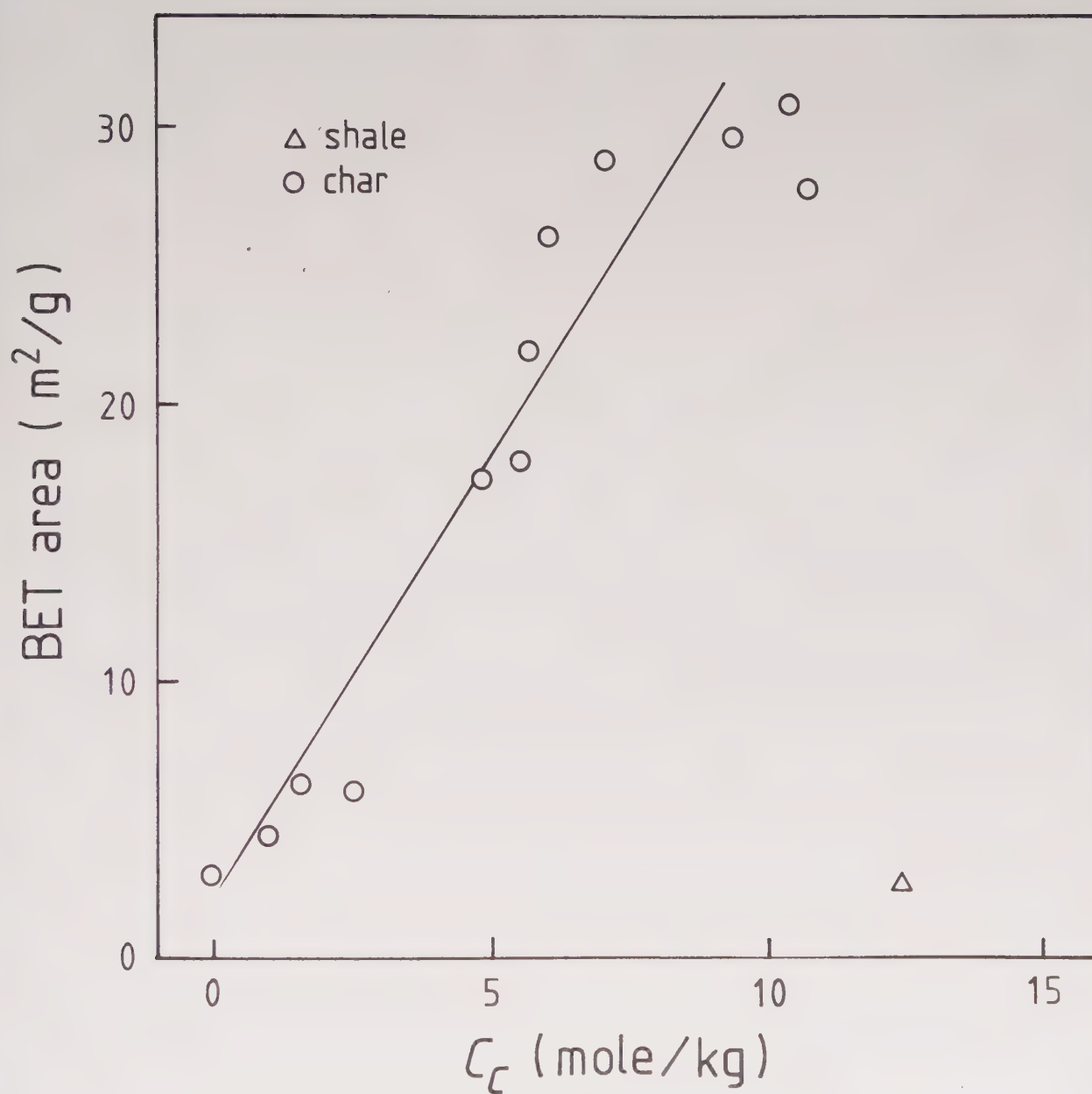


Figure 9

Ranstad shale. Steam gasification.

B.E.T. areas of raw shale and char against carbon content (moles C/kg).

APPLICATION OF CHEMICAL AND PHYSICAL OPERATIONS IN A
CIRCULATING FLUIDIZED BED REACTOR

Part 1 - Gasification of Uranium-bearing Black Shale

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ABSTRACT

This paper describes the development of a new reactor that operates with circulating fluidized beds. The bed mass recirculated acts as a heat carrier between two reaction chambers, within the same outer reactor shell. For solids circulation no moving parts such as valves or hoppers are used.

The reactor has been applied to the gasification of black shale, where the shale char itself is utilized as a heat carrier between an air-blown combustion zone and the gasification chamber. The segregation of the gas phases is very good, with a negligible crossflow between the reaction zones.

In the temperature range 750 - 900°C a medium BTU-gas is produced, with a temperature difference between the combustion and gasification chambers of about 50°C.

1. INTRODUCTION

In the design and development of processes for the conversion of solid fuels by gasification, economic advantages can be obtained, if the use of pure oxygen in the production of medium-BTU or synthesis gas could be replaced by indirect methods for the oxygen supply.

In the reactor design described here the energy for the gasification step is generated by combustion with air of part of the fuel in a circulating fluidized bed and thus the fuel char acts as a heat carrier of physical enthalpy. The reactor has originally been developed for the gasification of black shales, but the principle could also be applied to other fuels such as coal, peat and biomasses by using an inert bed mass as heat carrier.

Sweden is poor in high grade energy resources, but the central parts of the country have extensive deposits of uranium-bearing black shales and large amounts of peat are located in the northern provinces.

Recovery of the uranium from the shales, with its uranium content of 0.020 - 0.035 % has become commercially interesting. In this process a simultaneous utilization of the fossil energy of the kerogen present has been proposed. The organic content of the shale used in this investigation, from the Ranstad deposit is about 18 - 20 %.

Approximate and ultimate analyses are given in Table 1, and as can be seen from Table 1 almost 75 % of the shale consists of inorganic matter. The kerogen is mostly embedded in the voidage of the inorganic structure, which makes the shale char suitable both as a fuel and as a heat carrier in the circulation reactor.

2. APPARATUS

For the production of gas suitable for synthesis purposes or as industrial medium BTU fuel gas, the gas must be virtually nitrogen free. In the utilization of a circulating heat carrier, the combustion and the gasification zones have to have segregated gas phases. This can be accomplished by using moving part devices or, as in the reactor described, by circulating solids.

The reactor, which works on a small pilot plant scale at the Lund Institute of Technology, is shown in Figure 1. The apparatus has a diameter of 0.4 m (0.2 m in the bed zone) and a total height of 3 m. All of this equipment is constructed from low nickel stainless steel.

The raw shale is fed from a closed container through a screw feeder at a maximum rate of 50 kg/h into an annular bubbling fluidized bed (1), see Figure 1. This outer slit has a width of 3 cm and the bed fluidizes to a height of 80 cm. Here, the shale is devolatilized and gasified with steam. The char is discharged through an overflow (2) into a sampling hopper. Above the bed level the cross-sectional area is expanded by a factor 5.5 as an entrainment zone.

Incoming gases, steam and air are preheated in electrical heaters to about 350°C before entering the reactor.

In the bottom section of the reactor, the char is brought into the central combustion tube (7 cm in diameter), blown with air and operated as an entrained flow reactor. The solids transportation into the tube is accomplished by mean of the steam flow through the inlet (4) and the ejection effect of the air inlet nozzle (5). The steam flow (4) also acts as a diffusion bar of gases between the two reaction zones.

At the top of the combustion tube, the solids are separated from the flue gas by a static impeller cyclone. The char separated falls into the annular recirculation slit (6), (width 2.5 cm). In the lower part of the slit the char will form a non-fluidizing moving bed column, segregating the gas phases in the gasification and combustion chambers.

The gas phase segregation has been checked by trace gas tests at elevated temperatures. From these tests it was concluded that the cross flow of gas between the zones was very small. The gas leakage from the combustion tube into the gasification zone, which is important if the gas is to be used for methanol synthesis, could be neglected.

A quite small leakage from the gasification to the combustion tube could be observed at pressure drops over the gasification bed, in the order of or exceeding that of the combustion tube.

The level of the char column in the recirculation slit can be controlled by three pressure probes placed along the slit. At a given gas velocity in the combustion tube, the height of the column can be regulated by changing the absolute pressure above the gasification bed by means of the disc valve in the product gas outlet, as shown on the flow sheet of the pilot plant in Figure 2. For the estimation of the char recirculation, the slit is equipped with a probe.

The reactor operation is controlled, to a major extent by a minicomputer system. The combustion temperature and gas velocity are in this small scale reactor controlled by adding steam to the combustion air and simultaneously keeping a constant gas velocity in the tube for securing stable fluidizing conditions. For this purpose, the control valves shown in Figure 2 are used. To maintain adiabatic conditions in the reactor the computer also supervises four external heating coils. Finally, temperature logging at 24 points and an alarm function are also handled by the computer.

The control system is shown schematically on the flow sheet of the pilot plant in Figure 2.

The off-gases from the combustion/gasification chambers pass cyclones, before a part of the gas will be withdrawn for analysis. The gas samples are scrubbed and filtered before being pumped to an on line gas chromatography and IR-analyzing system that is described elsewhere (1).

3. RESULTS

Research and development work on the gasification of Ranstad shale have been under way for some years at the Lund Institute of Technology. The first tests were carried out in an externally heated bench-scale

fluidized bed reactor. From these runs a data base concerning devolatilization and fixed carbon gasification in steam and carbon dioxide was obtained. The results of this investigation are described in the references (1,2).

The test runs with the circulating fluidized bed reactor (CFBR) have been performed between 750 and 900°C gasification temperature, and with combustion temperatures up to 1 000°C. The upper limit of the combustion temperature is set by the ash agglomeration point around 1050°C. The char mean residence time has in all runs been 1 hour.

If the shale is to be used as a heat carrier in a fluidized bed reactor it must withstand mechanical strain. From Table 2, which summarizes sieve analyses and fluidization properties of the shale, the difference in the particle distribution between the feed shale and the char discharged is slight. The amounts of fly ash collected in the cyclones are about 10 - 15 % of the shale feed flow, of which 90 % is collected from the flue gas. As previously mentioned, the bulk flow of particles from the combustion tube is separated from the flue gas by a static impeller. The separation efficiency exceeds 99.5 %, based on the total amount of char recirculated. The particle distributions of the two fly ash streams are different from each other in the way that the particle size from the combustion zone is quite similar to the char distribution in Table 2, while the fly ash from the gasification zone holds no particles larger than 50 µm.

Over the temperature range investigated, 850 - 1000°C, the composition of the flue gas from the combustion tube is almost constant, with a dry basis analysis of 80 % N₂, <1 % O₂, 1.5 % CO, 16 % CO₂ and 2.5 % SO₂.

During the test runs the gasification temperatures and the temperature difference between the two beds were varied by changing the superficial velocity of the combustion air, and thereby changing the recirculation ratio and also the temperature difference. The recirculation ratios measured were found to be in the range of 40-65 times the shale feed flow depending on the combustion air velocity.

The air velocity in the combustion tube is limited to around 6 m/s. Higher velocities will result in a too low separation efficiency of the impeller cyclone. This restriction limits the reactor temperatures and to achieve gasification temperatures above 800°C the air was enriched with small amounts of oxygen. The highest partial pressure of oxygen used was 24 kPa.

The product gas obtained will hold medium BTU quality (16 - 22 MJ/Nm³). The gas composition and gas production (Nm³/kg shale) is shown as a function of temperature in Figure 3a for the CFBR, and for comparison for the externally heated bed in Figure 3b. As can be seen the fraction of pyrolytic hydrocarbons is higher, while the hydrogen and carbon oxides production are considerably lower in the CFBR, compared with the externally heated bed. The lower production of carbon oxides can be related mostly to the lower carbon concentration in the CFBR compared with the externally heated bed, where the char is only exposed to pure steam.

The difference in hydrogen production is explained by both the lowered reaction rate of fixed carbon as previously mentioned, but also by the pyrolytic hydrogen release from the kerogen being a slower process than the hydrocarbon devolatilization. The hydrogen pyrolysis, and probably also, to some extent, the carbon oxides release by pyrolysis will therefore not be completed before the shale particle is transported to the combustion tube. During combustion it is assumed that the most reactive parts of the kerogen structure will be preferably attacked by the oxygen and therefore a particle returning to the gasification zone will show a decreased reactivity compared with the pure steam gasification in the externally heated bed.

Figure 4 gives an energy balance of the reactor in a typical run at 840°C gasification temperature. As can be seen, only slightly above 20 % of the energy in the kerogen has been converted to chemical energy in the product gas. To make a fair judgement of the CFBR as gasification reactor, it must, however be compared with alternative modes of gasification. The drawbacks of the CFBR from an efficiency point of view compared with conventional oxygen blown designs are the heating up of the combustion-air nitrogen and the possibility of energy losses as

combustible gases in the flue gas. These drawbacks have to be weighted against the energy demand for oxygen manufacture. At the shale deposit at Ranstad, the development company Ranstad Skifferaktiebolag is operating an oxygen blown gasifier on a pilot plant scale (0.4 in diameter, 250 kg/h shale throughput (3)). At running conditions comparable with the CFBR a gasification efficiency of 25-30 % was obtained at 830-850°C. The low numbers for both the CFBR and the Ranstad pilot reactor can be related partly to shale being a low grade fuel and partly to non-optimized preheating systems and small scale effects. The incoming gases enter at rather low temperatures in both reactors and, additionally in the CFBR, the steam is fed in large excess because of the shallow gasification bed. Finally, the shale is not preheated. Experiments with preheating in a cyclone system have indicated possible preheating temperatures of 250°C, above which the kerogen starts to decompose.

4. REACTOR MODEL

For simulation, check-up of the test runs and scale-up calculations, a reactor model has been developed. Input data for the computer program can be summarized as:

- Char recirculation rate
- Shale and gas (steam, air) feed rates
- Temperatures of feed flows

The program will calculate mass and energy flow around the reactor according to the following list:

- Gas production and composition of the product and flue gas streams
- Char composition and amount of char discharged
- Enthalpies of all streams around the reactor

The complex pattern of operation for the CFBR does not allow a study of gasification kinetics, therefore kinetic data from runs in the externally heated bed have been used in the simulation of the CFBR behavior.

Furthermore, the calculations are based on the following assumptions about the reactor performance:

- Heat is transferred from the combustion tube to the gasification chamber only by the circulating char.
- The char is perfectly mixed in the reactor.
- Char and flue gas are in temperature equilibrium at the top of the combustion tube.

A flow sheet of the computer program is sketched in Figure 5. In Figure 6, the steady-state temperatures in the gasification and combustion zones are displayed against the ratio of char recirculation to shale feed flow at two different oxygen inlet pressures. As mentioned earlier, because of design reasons, oxygen had to be added to the combustion air in order to reach higher gasification temperatures. The result of the simulation with this oxygen load is shown by the dashed line. As expected, an increased recirculation decreases the temperature difference between the gasification and combustion zone.

To illustrate the possible range of operation for the process conditions in the pilot CFBR, the steady-state temperatures at different char residence times have been simulated and are shown in Figure 7. At low residence times, the heat production in the reactor is insufficient for heating up the solid feed flow, giving a low temperature in the gasification chamber. The gasification reactions are of minor importance below 750°C, where only pyrolysis contributes to gas production (1,2). At higher residence times, the carbon burn-out will be complete as also indicated in Figure 7. The quite narrow "window" of operation for the pilot CFBR can, in a commercial application be expanded by using a lower steam excess and an improved preheating.

In Table 3 the gas composition and gas production obtained by simulation at 780°C gasification temperature is compared with experimental findings in the CFBR.

To summarize the simulations, the pilot CFBR can be operated over a limited interval of temperature and char residence time. The out-put from the reactor model simulation has been shown to be in good agreement with the experimental findings.

4.1 SCALE-UP BY THE REACTOR MODEL

The translation of laboratory results to the design of a commercial scale unit is a delicate task in chemical engineering work. This becomes especially critical for fluidized beds because of their complex hydrodynamic behavior.

The experiments with the CFBR have demonstrated that the char can be used as a heat carrier, and that the solids circulation can be maintained without operational disturbance. For reasons discussed earlier, the potential as a chemical reactor can not be fairly judged from the experimental runs. The reactor model has therefore been used to calculate and to illustrate the effects of preheating temperatures, internal recirculation ratios and char residence times on the gasification efficiency and gas properties for a commercial scale CFBR.

In the calculations a reactor with a shale throughput of 40 ton/h at 1 h char residence time is outlined. The dimensions chosen for the reactor are summarized below.

- Outer diameter, gasification bed: 5 m
- Outer diameter, recirculation slit: 3.5 m
- Combustion tube diameter: 2.5 m

Table 4a gives the results of the calculation. From the table it can be observed that a preheating of the shale to 200°C, or an increased temperature of the inlet gases from 300°C to 500°C will have an equal effect on the gasification efficiency, with an increase from 22 % to about 27 % (case 1, 2, 3 in Table 4a). Increasing char residence time to 1.5 h will have an improved effect giving an increase from 32 % to 44 % (case 4, 5). Changing the char recirculation-ratio from 50 to 100, meaning that about 2700 tons of char is circulating per hour at 1.5 h char residence time, had just a minor influence and only increased the efficiency from 44 % to 45 %, (case 5, 6). In Table 4b, gas production is shown to increase considerably, compared with the experimental runs. The higher preheating temperatures and the increased char residence time does allow a much higher gasification temperature giving a higher gas production and a shift in the composition towards more hydrogen and carbon oxides.

The scale-up of fluidized bed reactors is not a very well understood problem and gas back mixing, together with a high steam conversion and thereby high partial pressures of the product gases could reduce the gas production calculated in Tables 4 a,b. A further development of the reactor model will take into consideration both these factors which are not accounted for in the present model.

5. CONCLUSIONS

The reactor principle proposed has been demonstrated to work on a small pilot plant scale with black shale as a fuel. The use of the shale char as circulating heat carrier will eliminate the need for pure oxygen for obtaining a nitrogen free product gas.

The reactor is very simple in its design, with no mechanical moving parts necessary for the solids circulation and gas phase segregation. Furthermore, the CFBR, with its separate heat generation and gasification zone will reduce the demand for carbon dioxide removal before methanol-synthesis, in contrast with oxygen blown gasifiers.

The gasification efficiency was found to be low, compared with what is normal in coal gasification. The difference is explained mainly by the extremely high ash content of the shale, and low preheating temperatures of the inlet gases. When compared with pilot plant results from a conventional oxygen blown fluidized bed gasifier also operating on Ranstad shale the efficiency of the CFBR was about 15 % lower at 840°C gasification temperature.

A simulation of a commercial scale CFBR-gasifier with the reactor model proposed indicated possible gasification efficiencies of 40 - 45 % using the same operation conditions as in the pilot plant runs, but higher gas inlet temperatures, a longer char residence time and a preheated shale feed.

ACKNOWLEDGEMENTS

The authors are grateful to the National Swedish Board for Energy Source Development for their financial support, and to Ranstad Skifferaktiebolag for their interest and co-operation during the course of this project.

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- 2) Bjerle I., Eklund H. Svensson O.; "Gasification of Swedish Oil Shale in a Fluidized Bed Reactor". Paper presented at the Symposium on the Gasification and Liquefaction of Coal, UN-Economical Commission for Europe, Katowice, Poland, April 23-27 1979.
- 3) Private communication, Mr Bo Oscarsson, Ranstad Skifferaktiebolag, S-520 50 Stenstorp, Sweden.

TABLE 1

Ranstad shale, analysis

Proximate analysis, wt %		Ultimate analysis		
		Kerogen (maf) ⁺⁺		Shale (mf) ⁺⁺
Moisture (as recieved)	5.0	% C	73.7	15.0
Volatile matter (mf)	13.0	% H	6.9	1.4
Fixed carbon (mf)	12.1	% O	8.5	1.7
Ash (mf)	74.9	% S	9.0	7.0 ⁺
Calorific heat of combustion: 27 MJ/kg kerogen, 6.6 MJ/kg shale				

+ 5.2 % pyritic, 1.8 % organic

++ mf: moisture free, maf: moisture- and ash free

TABLE 2

Ranstad shale, sieve analysis

D _p (mm)	Shale, wt %	Char ⁺ , wt %
2.0 - 1.0	3.4	3.7
1.0 - 0.80	5.7	5.0
0.80 - 0.63	31.7	31.2
0.63 - 0.40	35.1	36.6
0.40 - 0.20	19.2	19.2
0.20 - 0.10	4.2	3.7
0.10 - 0.05	0.5	0.3
< 0.05	0.2	0.3
Fluidization velocities: (air, 20 ⁰ C)		
Minimum fluidization	0.15 m/s	
Terminal velocity	3.2 m/s	

+ 900⁰C gasification temperature, 1 h char residence time

TABLE 3

Comparison, experimental CFBR run - reactor model simulation

Item	Experimental	Simulation
Char residence time (h)	1.0	1.0
Char recirculation ratio	40	40
Shale feed temperature ($^{\circ}\text{C}$)	20	25
Gas inlet temperatures ($^{\circ}\text{C}$)		
Air	260	260
Steam	350	350
Combustion temperature ($^{\circ}\text{C}$)	850	855
Gasification temperature ($^{\circ}\text{C}$)	780	795
Gasification efficiency (%)	18.0	17.0
Gas production ($\text{Nm}^3/\text{kg shale}$)	0.065	0.057
Gas composition (mole %)		
H_2	39	35
CO	9	11
CO_2	15	19
C_mH_n	27	23
H_2S	10	12

TABLE 4 A

Scale-up simulation of the CFBR

Case No	SIMULATION INPUT			SIMULATION OUTPUT		
	Shale feed temperature(^o C)	Air/Steam inlet temperature(^o C)	Char recirculation ratio	Char residence time(h)	Combustion temperature(^o C)	Gasification Gasification temperature(^o C) efficiency(%)
1	25	300	50	1.0 ⁺	820	785 22
2	200	300	50	1.0 ⁺	850	815 27
3	25	500	50	1.0 ⁺	850	810 26
4	200	500	50	1.0 ⁺	880	840 32
5	200	500	50	1.5 ⁺⁺	975	925 44
6	200	500	100	1.5 ⁺⁺	965	940 45

Combustion air velocity: 6 m/s, steam velocity: 0.5 m/s

+ Shale feed: $4 \cdot 10^4$ kg/h++ Shale feed: $2.7 \cdot 10^4$ kg/h

TABLE 4 B

Gas production and composition in some scale-up simulations

	Case 1	Case 6
Gas production, (Nm ³ /kg shale)	0.089	0.23
Gas composition, (mole %)		
H ₂	43	54
CO	15	17
CO ₂	19	20
C _m H _n	15	6
H ₂ S	8	3

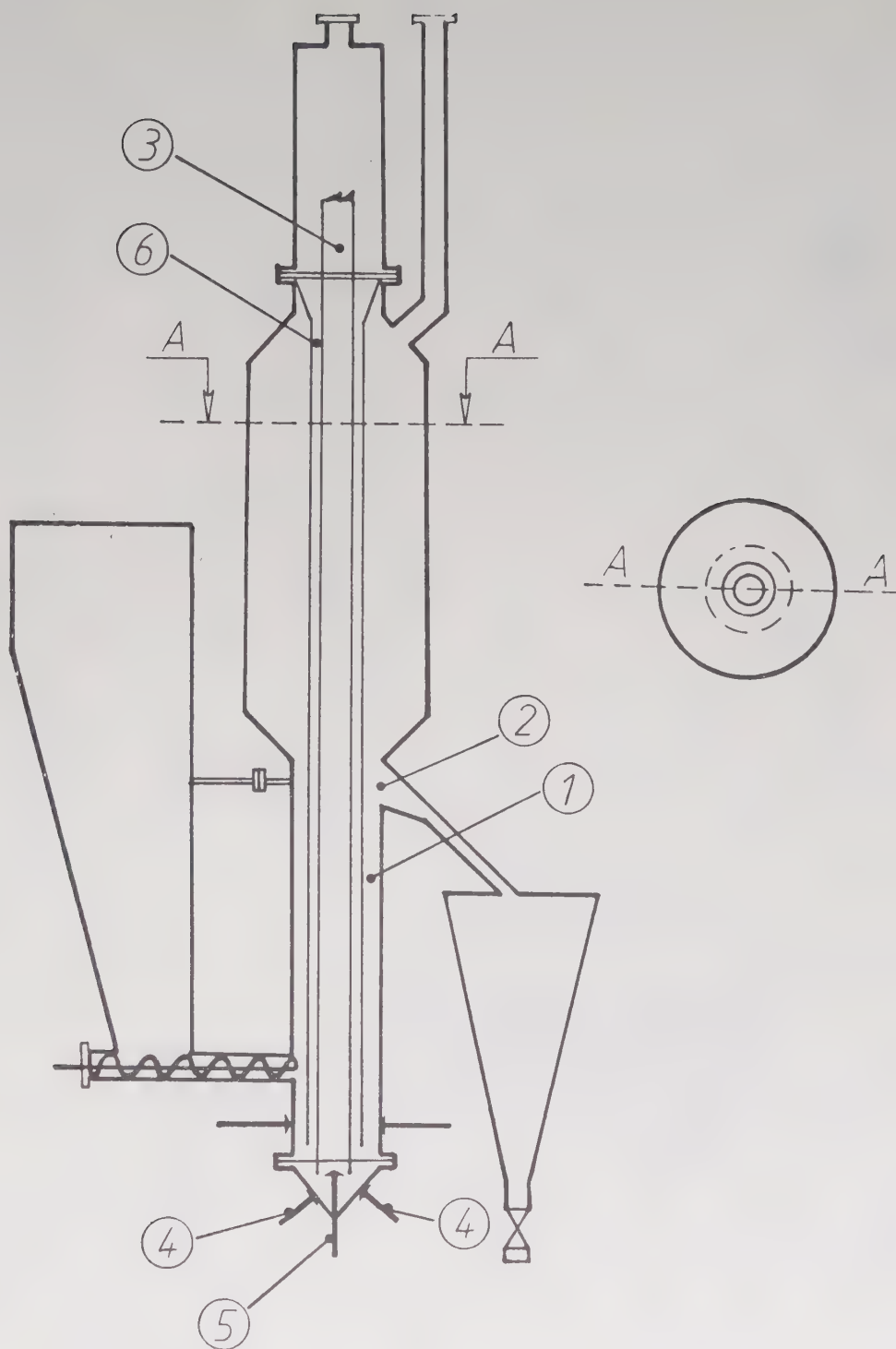


Figure 1

The Circulating Fluidized Bed Reactor.

- | | |
|---------------------------|----------------------|
| 1. Bubbling fluidized bed | 2. Overflow |
| 3. Riser tube | 4. Steam inlet |
| 5. Air inlet | 6 Recirculation slit |

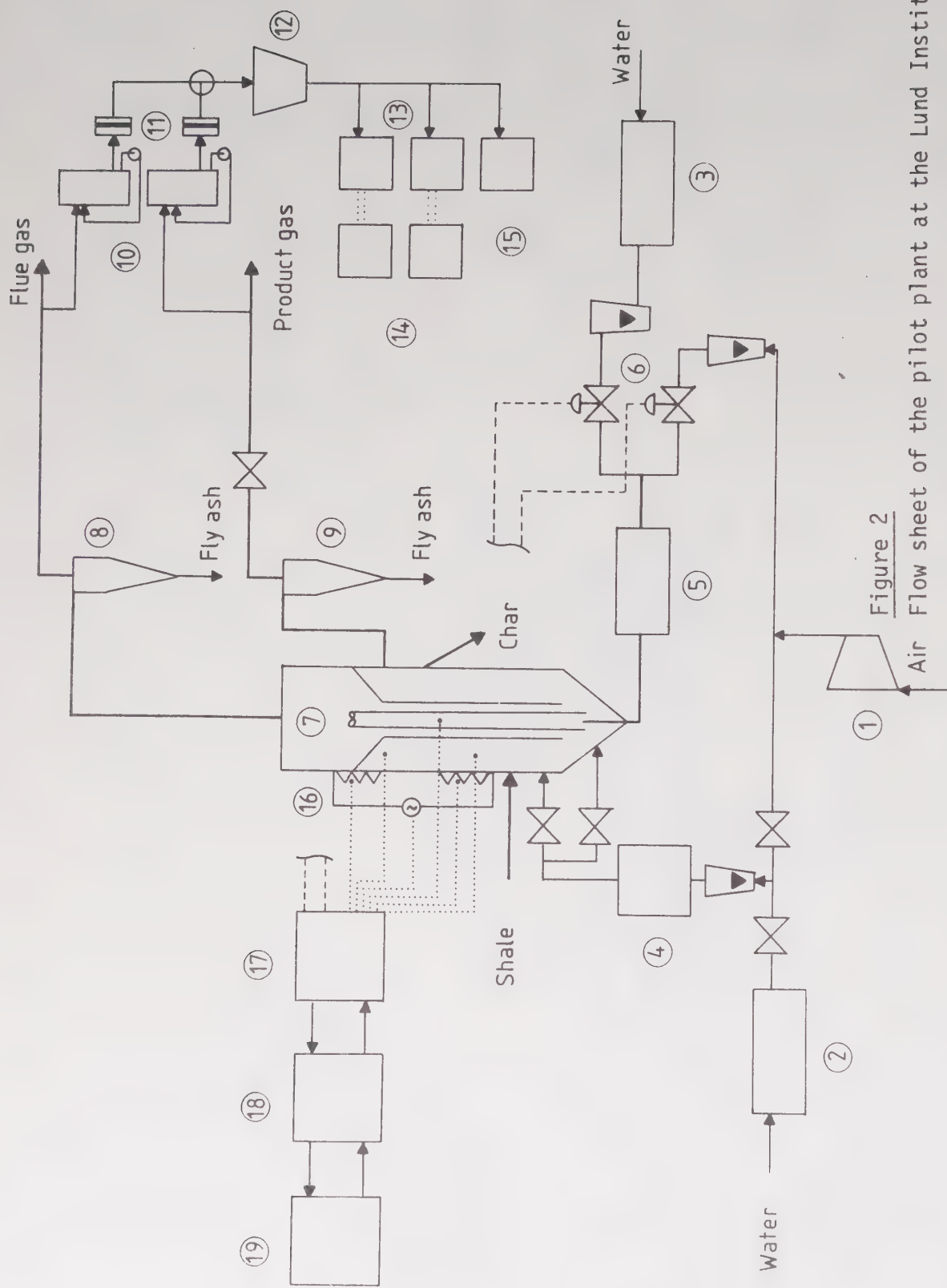


Figure 2

Flow sheet of the pilot plant at the Lund Institute of Technology.

1. Air compressor
2. Steam generator
3. Gas preheater
4. Gas preheater
5. Gas preheater
6. Gasification reactor
7. Gasification reactor
8. Cyclone
9. Scrubbers
10. Filters
11. Gas chromatographs
12. Microprocessor
13. Heating coils
14. D/A interface
15. Printer

3. Steam generator
6. Control valves
9. Cyclone
12. Gas pump
15. IR-analyzer
18. Mini computer

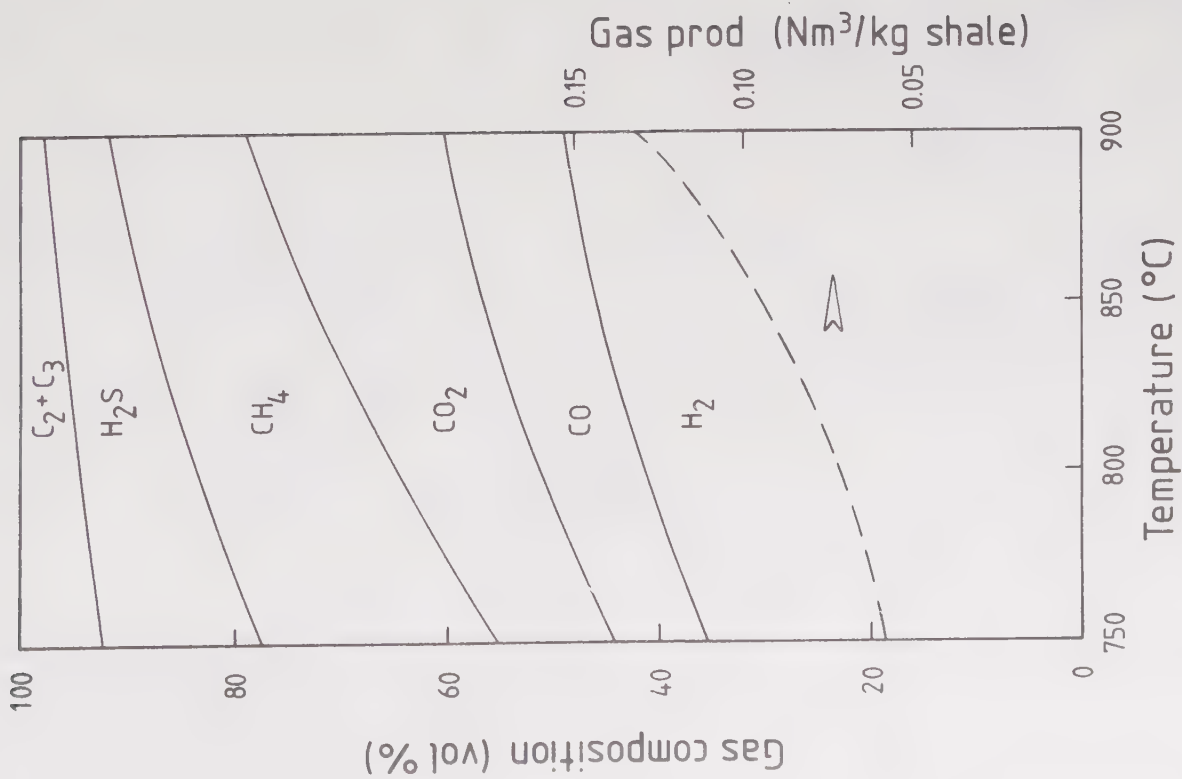


Figure 3a

Ranstad shale. Gas composition and production for the CFBR as a function of temperature at 1 h char residence time.

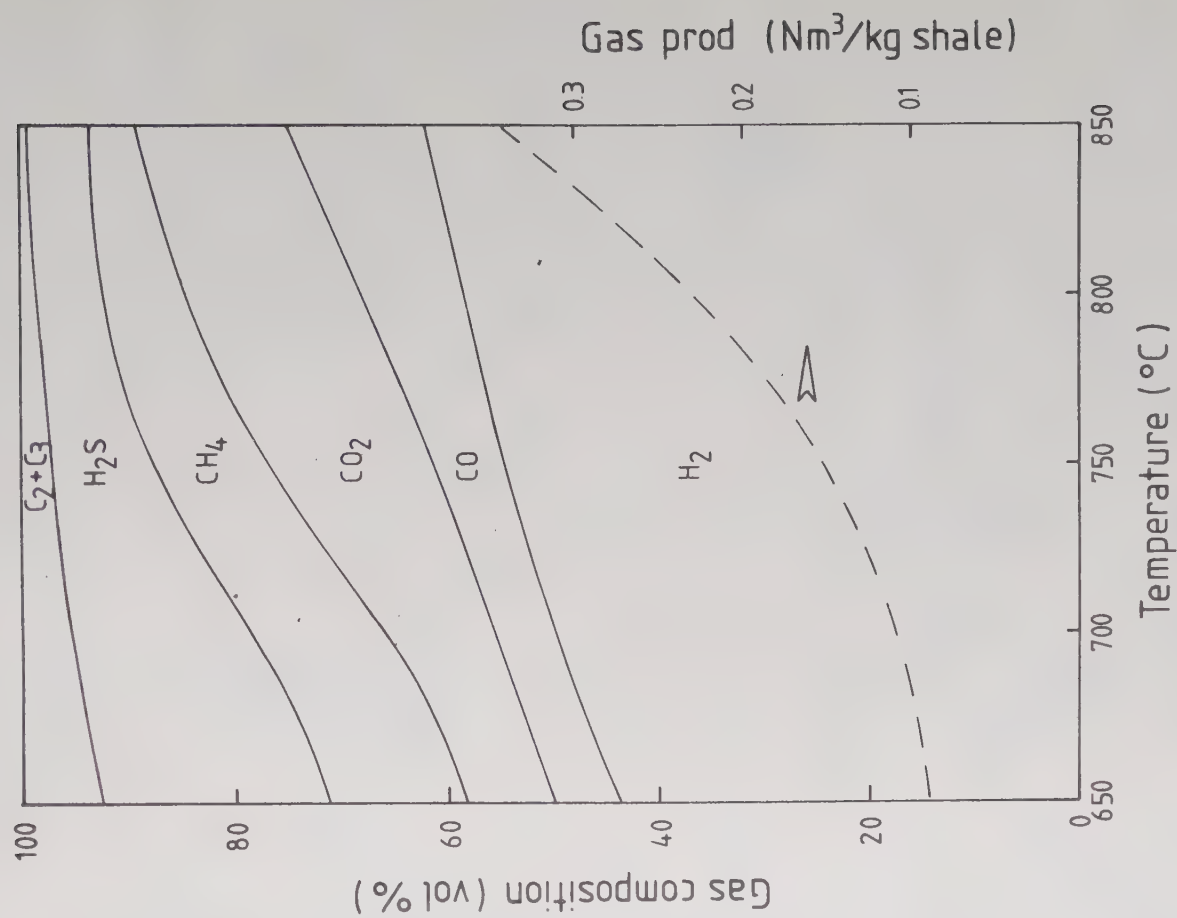


Figure 3b

Ranstad shale. Gas composition and production for the externally heated fluidized bed as a function of temperature at 1 h char residence time.

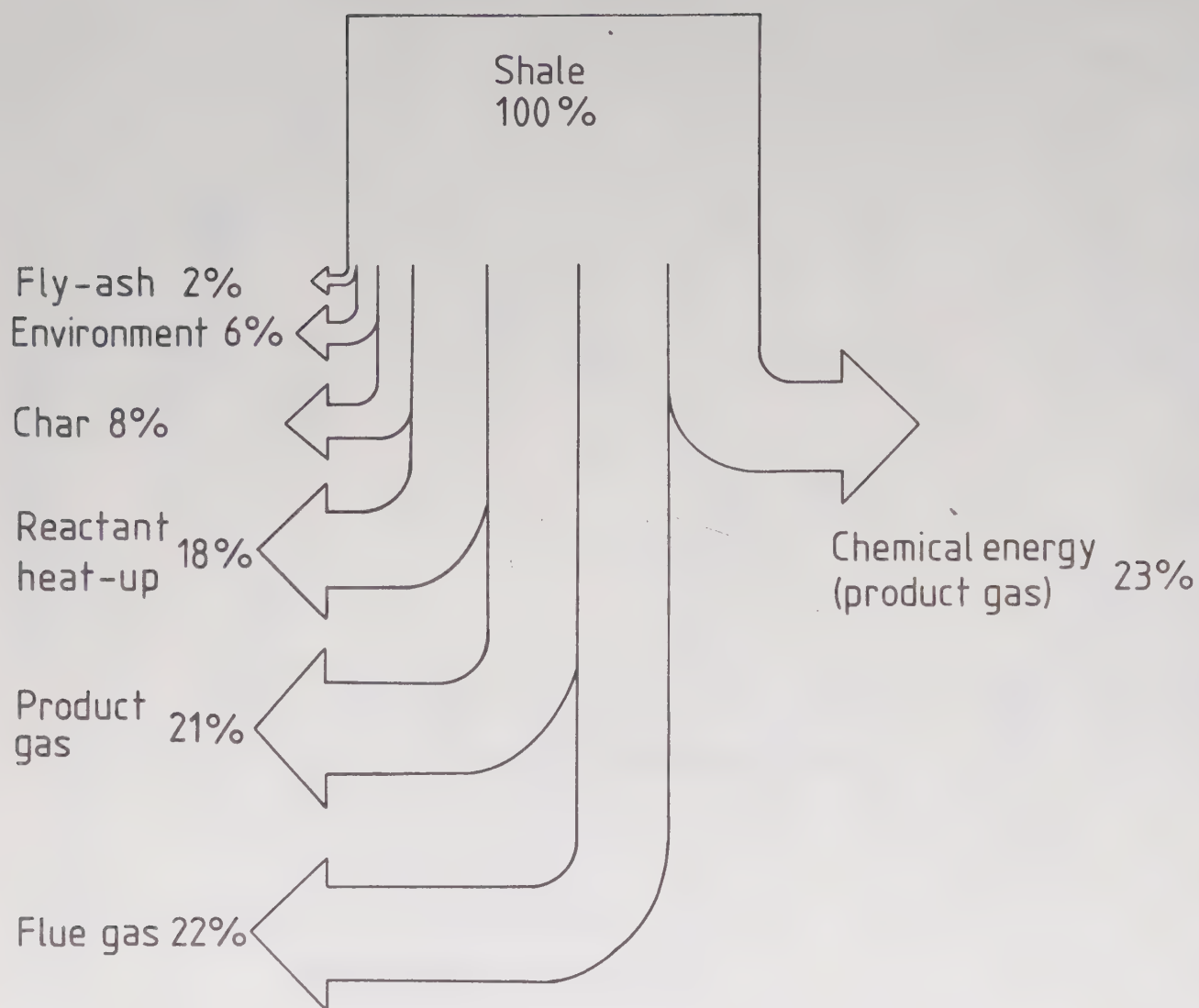


Figure 4

Energy flow for a typical test run in the CFBR at 840 °C and 1 h char residence time.

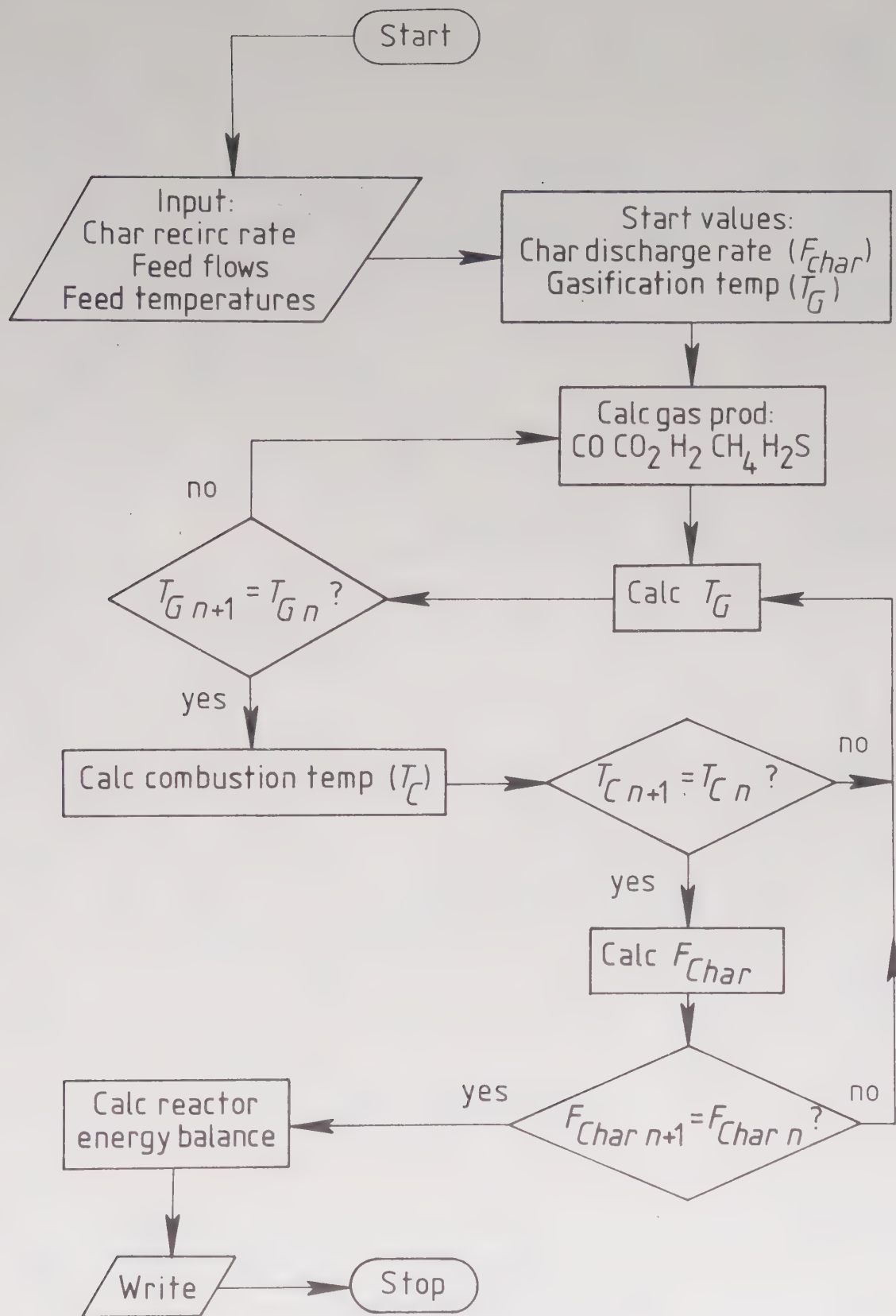


Figure 5

Flow sheet of the computer program
for the CFBR reactor model.

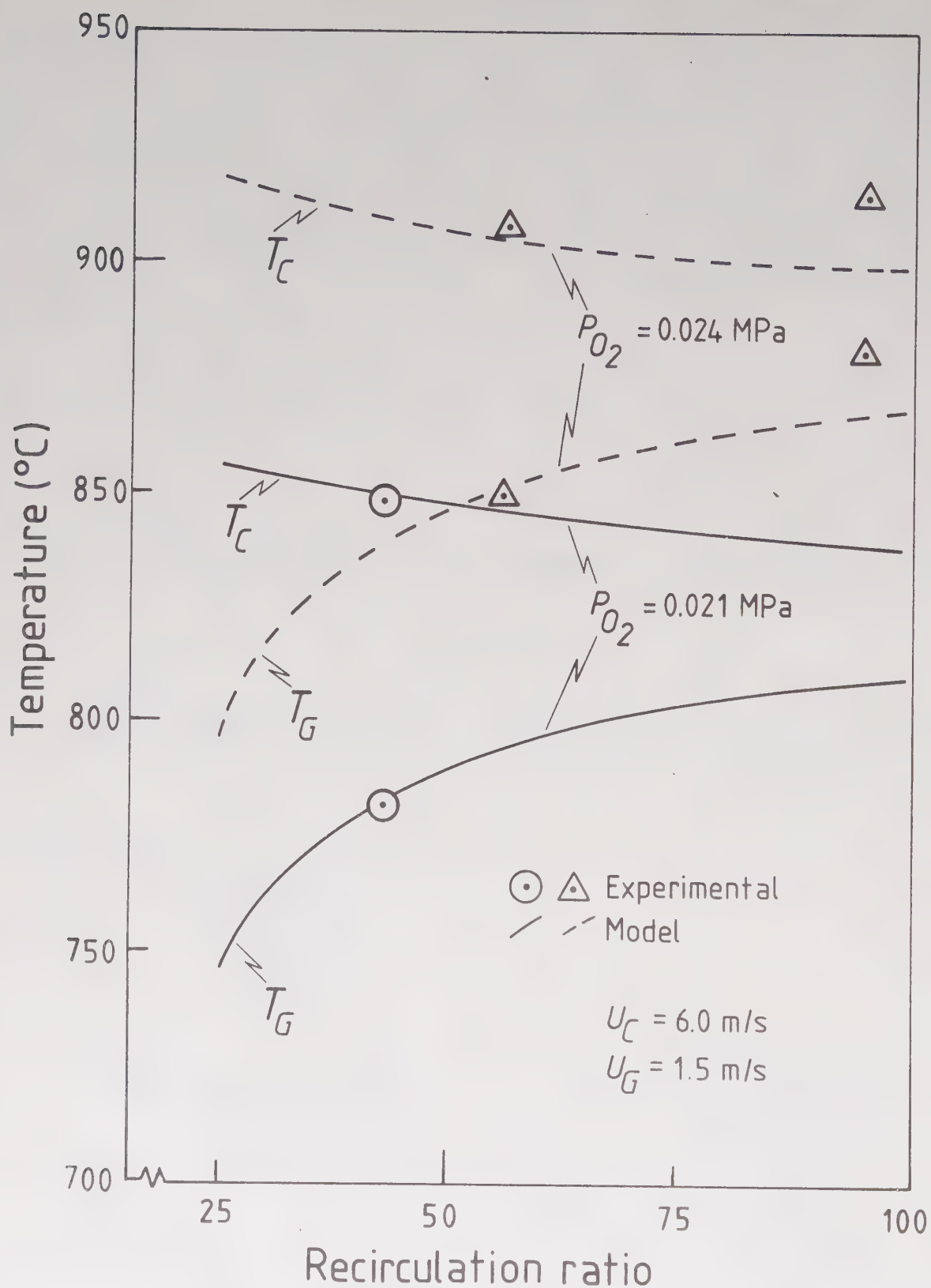


Figure 6

Reactor model simulation compared with test runs.

Steady state temperatures as a function of char recirculation

ratio, u_c = superficial air velocity, u_g = superficial steam velocity.

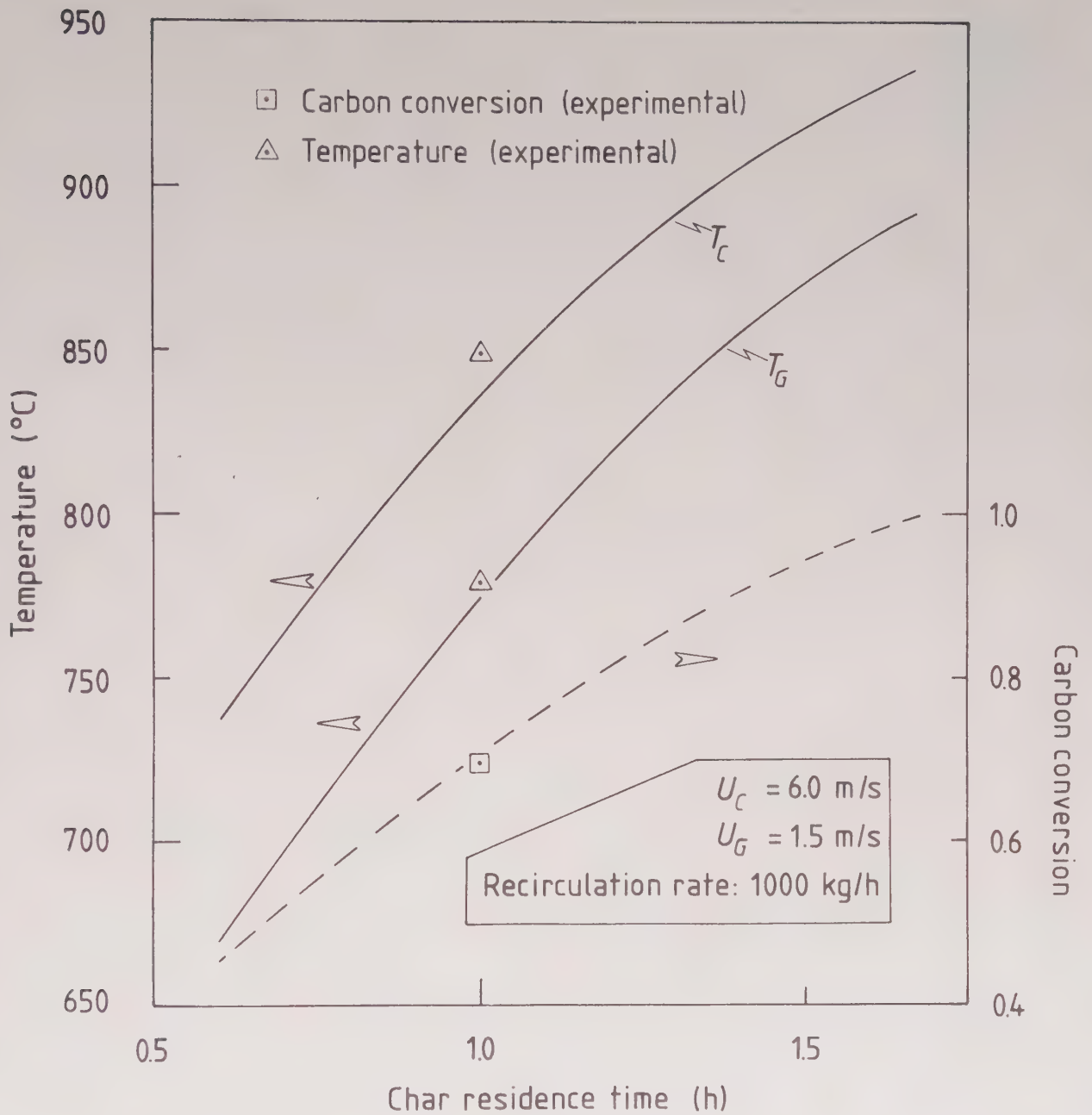


Figure 7

Reactor model simulation compared with test runs.

Steady state temperatures and carbon conversion as a function of char residence time, u_c = superficial air velocity, u_g = superficial steam velocity.

THERMOGRAVIMETRIC ANALYSIS OF SWEDISH SHALE CHAR

Kinetics of the Steam-Carbon and Carbon Dioxide-
Carbon Reactions

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ABSTRACT

The kinetics of gasification of shale char from the Swedish Ranstad deposit have been investigated by thermogravimetric analysis.

The reaction rate of fixed carbon can be described by modified Langmuir-Hinshelwood expressions. Similar to coal, retarding effects of hydrogen and carbon monoxide were found. The catalytic effect of impregnation with potassium and calcium salts was found to be of minor importance in the temperature interval 850 - 940 °C.

1. INTRODUCTION

The Swedish shale deposits with its uranium and kerogen content are considered for utilization. Due to a low oil yield and a high sulphur content, the gasification route offers advantages for the kerogen recovery.

Research and development in the field of gasification has so far been conducted in fluidized bed reactors of bench scale and small pilot plant size. Results from these investigations are reported elsewhere, Bjerle et al. (1979) and Berggren et al. (1979).

The tests in the bench and small pilot reactors have been useful in the study of the gasification process and in evaluating the feasibility of using fluidized bed reactors for this process.

For more specific studies of the fixed carbon gasification, thermogravimetry is an applicable method. In this article, the kinetic conditions for the shale char gasification with steam and carbon dioxide in the hydrogen and carbon monoxide atmospheres have been examined. Additionally, the catalytic effects of potassium and calcium salts were studied.

2. APPARATUS AND EXPERIMENTAL

The thermogravimetric equipment (TG) used is schematically shown in Figure 1. The unit consists of a standard Cahn 2000 microbalance, together with a furnace section, specially designed for operation in steam atmosphere.

The microbalance is built into a stainless steel shell to allow operation at moderate elevated pressures. Non-condensable reactant gases are measured with rotameters and preheated before entering the furnace. When operating with steam, the water flow is controlled by a step-motor driven syringe. To prevent gas leakage and to avoid steam

condensation, a nitrogen flow is introduced in the upper weight chamber. The rate is about 10 % of the total flow through the furnace.

The stainless steel furnace consists of an outer, water-cooled jacket and an inner, thin-walled tube, surrounded by the heating coil. The temperature of the coil is supervised by a PI-controller, and measured by a thermocouple placed in a slit between the wall and the coil. The temperature within the furnace is registered by a thermocouple placed in the center of the inner tube and about 3 mm below the sample basket.

To protect the thermocouple from radiation, it is covered by a thin plate at the top. The sample basket is also covered by a plate placed 5 mm above the basket to reduce radiation losses from the sample.

The maximum heating rate of the sample, which is measured by an extra thermocouple placed in the sample basket, is 20 K/s. No difference in the heating rate can be observed between the thermocouple embedded in the sample and the one placed in the furnace center previously mentioned.

After removal from the furnace the gases are cooled in a water cooled condenser, where steam and tars are separated from the rest of the gas.

During a run, a sample of about 10 - 20 mg of shale char is loaded in the sample basket. The temperature is raised to 150 °C and the sample is dried to a constant weight in nitrogen atmosphere. Then the temperature is further raised to the desired level at the rate of 20 K/s mentioned earlier. Simultaneously the reactant gas mixture is introduced and the weight loss is registered.

3. RESULTS

3.1 GASIFICATION OF SHALE CHAR IN THE PRESENCE OF H_2O , H_2 , CO_2 , AND CO

From nonisothermal thermogravimetric tests on Ranstad shale it is known from Bjerle et al. (1979) that the steam-carbon and the carbon dioxide-carbon reactions start above 700 °C and 800 °C respectively. The char gasification tests have been performed at atmospheric pressure with temperatures between 800 and 975 °C in the steam case and between 850 and 990 °C in the carbon dioxide case.

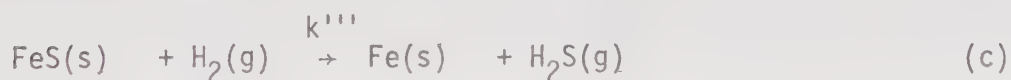
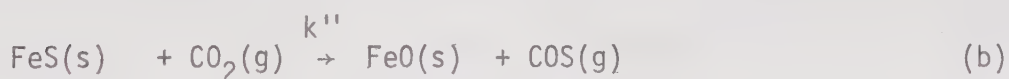
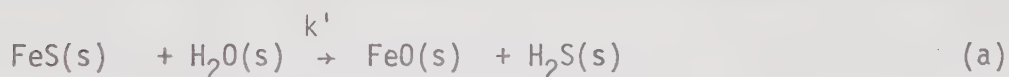
The char samples were manufactured by crushing raw shale to less than 1 mm, and then pyrolyzing in nitrogen atmosphere at 700 °C for 3 hours. The pyrolyzed char was then further crushed to less than 0.3 mm and well mixed to avoid inhomogenities in the small sample quantities used in the TG runs.

Table 1 summarizes proximate and ultimate analysis of the raw shale, and ultimate analysis of the pyrolyzed char.

3.1.1 Reactions of sulphur in the char

As can be observed from the char analysis in Table 1, the sulphur content in the char is slightly above 4 %. The weight loss registered during the runs therefore show contributions from both carbon and sulphur reactions. To obtain the correct reaction rate of carbon, the weight loss related to sulphur has to be accounted for in the evaluation of the weight loss curve. With the assumption that the sulphur is bound as FeS after the pyrolysis, the reaction rate of carbon can be calculated, if kinetic data for the FeS reactions with H₂O, H₂, CO₂ and CO are known.

FeS can react according to the formulas;



The reaction rate of FeS with the gases in formulas (a) to (d) have been investigated and kinetic parameters were obtained by fitting the rate to a first order expression with respect to sulphur;

$$-\frac{dW_S}{dt} = k_0 \cdot e^{-E_A/RT} \cdot W_S \quad (1)$$

Samples of flotation pyrite with an FeS_2 content of 96.5 % were heated in nitrogen atmosphere in the TG apparatus to 700 °C until the weight curve indicated a quantitative loss of the free sulphur atom in the pyrite. Afterwards the temperature was adjusted to the level desired and the reactive gas (eg. H_2O , H_2 , CO_2 or CO) was introduced. During the runs it was found that reaction (d) did not occur at temperatures below 1000 °C, and as a rule the other reactions were quite slow. This was also stated by Attar (1978) in his review of coal-sulphur reactions. Attar also concluded the negligible influence of reaction (e) below 1000 °C. The apparent kinetic constants for reactions (a) to (c) are summarized in Table 2.

The weight curve during gasification in steam and carbon dioxide can be subdivided into different parts, as schematically described by Figure 2. In Figure 2 the weight loss curve is shown together with the influence of the sulphur reactions on the residual weight of the sample. When gasifying in steam and carbon dioxide atmosphere, the sample weight will decrease due to the gasification reactions of carbon and sulphur, but simultaneously there will be an increase in weight due to iron oxide formation according to reactions (a) and (b), which are to be accounted for in the evaluation. In the hydrogen atmosphere, the observed weight loss has only to be corrected for the release of sulphur as H_2S .

From Figure 2 the weight of residual carbon in steam or carbon dioxide atmosphere can be written as;

$$W_C = W - W_{\text{ash}} - \frac{1}{2}(W_{\text{OS}} + W_S) \quad (2)$$

with the weight of sulphur expressed as

$$W_S = W_{\text{OS}} e^{-k' \cdot t} \quad (3)$$

Combining (2) and (3) yields

$$W_C = W - W_{\text{ash}} - \frac{1}{2} W_{\text{OS}} (1 + e^{-k' \cdot t}) \quad (4)$$

W_C can be transformed into carbon concentration

$$c_C = \frac{1000}{12} \cdot \frac{W_C}{W} \quad (5)$$

A combination of (4) and (5) yields an expression of c_C in observational terms only;

$$c_C = \frac{1000}{12W} \left[W - W_{ash} - \frac{1}{2} W_{OS} (1 + e^{-k' \cdot t}) \right] \quad (6)$$

Derivation of (6) with respect to time gives the reaction rate of carbon as;

$$r_C = \frac{dc_C}{dt} = \frac{1000}{12W^2} \left[W_{ash} \frac{dW}{dt} + \frac{1}{2} W_{OS} \left((1 + e^{-k' \cdot t}) \frac{dW}{dt} - k' \cdot e^{-k' \cdot t} \right) \right] \quad (7)$$

In analogy, carbon and sulphur weights in hydrogen atmosphere are described by

$$W_C = W - W_{ash} - W_S \quad (8)$$

$$W_S = W_{OS} e^{-k''' \cdot t} \quad (9)$$

The carbon concentration can be written as;

$$c_C = \frac{1000}{12W} (W - W_{ash} - W_{OS} e^{-k''' \cdot t}) \quad (10)$$

By derivation the reaction rate is found as;

$$r_C = \frac{1000}{12W^2} \left[(W_{ash} + W_{OS} e^{-k''' \cdot t}) \frac{dW}{dt} + W_{OS} W k''' e^{-k''' \cdot t} \right] \quad (11)$$

3.1.2 Reaction in steam and carbon dioxide atmospheres.

For gasification reactions it has been shown by Wicke et al. (1956) that diffusional effects are of minor effect below 1000 °C, and the chemical reaction can be considered as rate controlling. In large excess of steam on carbon dioxide eg. negligible partial pressures of the reaction products H_2 and CO and far from equilibrium, the rate equation can be expressed as;

$$-(r_C)_{H_2O} = k_1 \frac{k_2 p_{H_2O}}{1 + k_2 p_{H_2O}} \cdot c_C \quad (12)$$

$$-(r_c)_{CO_2} = k_4 \frac{k_5 p_{CO_2}}{1+k_5 p_{CO_2}} c_c \quad (13)$$

Rearrangement of (12) and (13) yield equations linear in $1/p_{H_2O}$ and $1/p_{CO_2}$;

$$-(\frac{c_c}{r_c})_{H_2O} = \frac{1}{k_1 k_2} \cdot \frac{1}{p_{H_2O}} + \frac{1}{k_1} \quad (14)$$

$$-(\frac{c_c}{r_c})_{CO_2} = \frac{1}{k_4 k_5} \cdot \frac{1}{p_{CO_2}} + \frac{1}{k_4} \quad (15)$$

The constants will all follow an Arrhenius type temperature dependence

$$k_i = k_{i0} e^{-E_A/RT} \quad (16)$$

The constants k_1 and k_4 increase with temperature as they represent the chemical reaction step. The other constants can either increase or decrease with temperature while they describe adsorption/desorption kinetics.

To determine the constants in equations (12) and (13), the partial pressure dependence has to be measured at different temperatures.

The experimental result in $H_2O - N_2$ and $CO_2 - N_2$ mixtures are displayed in the Figures 3 and 4, from which the temperature dependence of the constants can be estimated in an ordinary Arrhenius plot as shown in the Figures 5 and 6.

The preexponential factors and the activation energies obtained are summarized in Table 3.

3.1.3 Reactivity in the presence of hydrogen and carbon monoxide.

The retardation effects of the reaction products from the gasification, e.g. H_2 and CO , are well known in literature. The investigations made by Gadsby et al. (1946) and Long and Sykes (1948), show that the inhibitative effects of hydrogen and carbon monoxide were considerable in both the steam - carbon and the carbon dioxide - carbon systems.

They concluded the retardation effect of hydrogen by both the steam and carbon dioxide gasification. Carbon monoxide on the other hand was found to slow down the reaction rate in the carbon dioxide case only. This was explained in terms of different types of active sites, attacked by steam and carbon dioxide respectively, present on the carbon surface. Hydrogen is adsorbed on both types of sites, while carbon monoxide is adsorbed only on the sites active for the carbon - carbon dioxide reaction.

Furthermore it was stated that the retardation effects observed by gasification in steam - carbon monoxide mixtures could be related to hydrogen produced by the shift reaction. The shift reaction was shown to proceed at a rate considerably exceeding that of the fixed carbon gasification reactions. Finally, the data could be fitted to an ordinary Langmuir-Hinshelwood expression.

These findings were to a great extent contradicted by Hedden and Löwe (1967), who found an inhibitive effect of carbon monoxide also in the steam - carbon system. With their carbon samples, very pure graphite, the shift reaction was not occurring.

The inhibitive effect of carbon monoxide in the carbon dioxide - carbon reaction was shown to be non linear in the carbon monoxide partial pressure and thus, the reaction rate could not be expressed by a usual Langmuir-Hinshelwood equation. This effect was also qualitatively stated by Hedden et al. (1959). The data of Hedden and Löwe were well approximated by a square root dependence of the carbon monoxide pressure. It can thus be concluded that the results obtained so far are contradictory to each other on several points, and that the properties of the coal used is of particular importance.

As to the shale char, tests have been run at different temperatures with mixtures of H_2O/H_2 , H_2O/CO , CO_2/CO and CO_2/H_2 . Retarding effects of hydrogen and carbon monoxide were observed in both the steam and the carbon dioxide system. The true origin of this is very difficult to trace, e.g. is it carbon monoxide or is it to a major extent hydrogen indirectly produced by the shift reaction which is the retarding agent in the steam - carbon monoxide runs. For the carbon dioxide - hydrogen mixtures the situation is similar.

From kinetic studies of the shift reaction now in progress and from results from Bjerle et al. 1979, it can be stated that the shift reaction

occurs over shale char, and at a rate exceeding the fixed carbon reactions with more than a factor 10. Having this in mind it could be reasonable to assume the retardation observed in the H_2O/CO and CO_2/H_2 runs to be effects of hydrogen and carbon monoxide produced by the shift reaction. This reaction will thereby occur on the microstage within the pore structure of the char, whereby the local gas composition even at equilibrium can differ from that of the gas bulk. A gas analysis can not be used in the identification of the retarding compound since only a fraction of the gas mass penetrates the char structure.

Disregarding the local conditions, it is the bulk properties which are observable, and to which the correlation of the kinetic parameters have to be referred.

The inhibitative effects of CO and H_2 are included in both equation (17) and (18) below, even if, on the micro level, the conditions are such that mainly one component is active in each system.

In the runs with the H_2O/CO and CO_2/CO mixtures it was found that the data could not be fitted to a linear partial pressure dependence of carbon monoxide. As previously mentioned, this was also the case in the investigation by Hedden and Löwe (1967), where a square-root dependence could describe the experimental material.

In the shale case it was found that the deviation from non linearity became very marked at carbon monoxide partial pressures exceeding 30 kPa. In the steam and carbon dioxide systems an exponent of 0.25 and 0.05 respectively was found to fit the experimental data.

The reaction rate in the steam - carbon and the carbon dioxide - carbon systems are described by the expressions;

$$-(r_c)_{H_2O} = k_1 \frac{k_2 p_{H_2O}}{1 + k_2 p_{H_2O} + k_3 p_{H_2} + k_3' p_{CO}^{0.25}} \cdot c_C \quad (17)$$

$$-(r_c)_{CO_2} = k_4 \frac{k_5 p_{CO_2}}{1 + k_5 p_{CO_2} + k_6 p_{CO}^{0.05} + k_6' p_{H_2}} \cdot c_C \quad (18)$$

The exponents found, deviate strongly from a linear dependence, and it can be stated that the mechanism of retardation for carbon monoxide is different from that of hydrogen. In the case of hydrogen the chemisorption can be satisfactorily expressed with the Langmuir isotherm. For carbon monoxide it can be assumed that the retardation is a combined effect of chemisorption and electronic interaction between the adsorbed molecule and the carbon gitter, as proposed by Hedden et al. 1959. They explain the relatively stronger retardation at low carbon monoxide pressures with the capability of carbon monoxide to act as an electron donator to the carbon gitter.

The dissociation rate of carbon dioxide on the carbon surface is depending on the number of free electrons in the gitter, e.g. with a decreasing number of free electrons, the dissociation is increased. With increasing occupation of carbon monoxide on the surface the number of free electrons in the gitter increase, implying an increased retardation, but also a decreased driving force for additional electron donation. The influence of the electron donation step will therefore be weaker with increasing carbon monoxide partial pressure.

A comparison of the exponents of carbon monoxide between the H_2O/CO and the CO_2/CO runs shows a higher exponent in the H_2O case which can be taken as an indirect retarding effect of hydrogen from the shift reaction.

The runs with CO_2/H_2 mixtures showed a slight tendency to the same partial pressure dependence as stated for carbon monoxide. This is in agreement with the previous discussion, since carbon monoxide is produced both by the Boudouard and the shift reaction. The deviation was however of that order that a linear partial pressure dependence will still fit the data satisfactorily.

With the assumption that steam and carbon dioxide react in parallel, the total rate of carbon gasification in the presence of steam, hydrogen, carbon dioxide and carbon monoxide can be written as;

$$-(r_C) = \left[k_1 \frac{k_2 p_{H_2O}}{1 + k_2 p_{H_2O} + k_3 p_{H_2} + k_3' p_{CO}^{0.25}} + k_4 \frac{k_5 p_{CO_2}}{1 + k_5 p_{CO_2} + k_6 p_{CO}^{0.05} + k_6' p_{H_2}} \right] c_C \quad (19)$$

To check this equation, runs were performed at different temperatures and partial pressures of steam, hydrogen, carbon dioxide and carbon monoxide. The results of the experiments with the reaction rate expressed as (r_C/c_C) are summarized in Table 4 and correspond relatively well with the calculated rates.

3.2 INFLUENCE OF POTASSIUM AND CALCIUM SALTS ON THE GASIFICATION RATE.

Due to the slow reaction rate of fixed carbon it can be beneficial to use catalysts. Several investigations have recently been published, showing that the reaction rate can be affected by catalytic agents, Peter et al. (1976), Jalan and Rao (1978), Veraa and Bell (1978), Bernando and Trimm (1979), Otto et al. (1979) and Yokohama et al. (1979).

Most of these works studied the effects of impregnating the coal itself, while Peter et al. (1976) dissolved the catalyst in the steam under high pressure. As coal gasification is a large scale process, the catalyst must have certain properties to be feasible. It must be inexpensive and/or easily recovered without great losses. For commercial applications, this excludes many catalysts proposed in academic literature.

Much of the work in the area of catalytic coal gasification is performed by impregnation with alkali metal salts, but also the catalytic capacity of the ash constituents are important as pointed out by Otto et al. (1979).

The ash content of the shale char is extremely high and many elements with known catalytic power are present in the ash as shown in Table 5.

To get an indication of the catalytic properties of the ash, kerogen and sulphur free ash was ground to less than 20 μm particles and mixed with graphite powder to a 1:1 mixture on weight basis in a water slurry. The slurry was dried and gasified with steam ($p_{\text{H}_2\text{O}} = 50 \text{ kPa}$, $T = 1173 \text{ K}$) and the reaction rate was compared with that of pure graphite. A rather low increase of 20 % over the uncatalyzed case was observed. This rather weak influence of catalysis from the ash can be an effect of segregation of the coal from the ash in the microstage. The mechanical mixing of the coal and ash can never be as effective as that of the kerogen in the

inorganic matrix of the natural shale. Another possibility is a limited catalytic activity of the ash. This is because a majority of the potassium content may be bound to the silica matrix as feldspar.

In summary, the runs showed a catalytic influence from the shale ash which should be stronger in natural shale. However, no quantitative conclusions about its effect could be drawn.

The effects of adding catalytic agents by impregnation of prepyrolyzed char with potassium hydroxide, potassium sulphate and calcium hydroxide have also been studied.

The choice of potassium is besides its documented catalytic activity based on the possibility of utilizing potassium recovered from the shale ash in a combined metal extraction and gasification process. The use of calcium can be justified in that large quantities of overburden limestone must be removed before mining.

Shale chars prepyrolyzed in nitrogen at 850 °C for 6 hours were impregnated with solutions of the salts giving catalyst contents of 0.1 and 1 % by weight. The samples were gasified with steam ($p_{H_2O} = 50$ kPa) and the reaction rates are displayed in Figure 9. The data obtained show a limited effect of the impregnation which gave roughly 1.5 - 2 times higher reaction rate. It can also be seen that there is no conclusive difference between potassium and calcium in catalytic activity, nor is there an increase in reaction rate with increasing catalyst content.

To summarize, the alkali salt impregnation increased the reaction rate, but the effect was not so high that it can be considered feasible from a technical point of view. Such a pretreatment of the shale considerably contributes to the technical complexity of the gasification process.

3.3 COMPARISON WITH FLUIDIZED BED DATA

As mentioned earlier the reactivity of Ranstad shale has been studied in fluidized bed reactors of laboratory scale. In these runs the kinetics of shale gasification in steam and carbon dioxide atmosphere were obtained. The rates can be fitted to Langmuir - Hinshelwood expressions identical with the equations (12) and (13).

In Figures 10 and 11 the data of the TG-runs are compared with fluidized bed kinetics at constant partial pressures of steam and carbon dioxide of 50 kPa. For both steam and carbon dioxide atmospheres, the TG-data show higher apparent activation energies than those of the fluidized bed.

In the temperature intervals where the Arrhenius plots overlap the TG data also show higher reactivity than those of the fluidized bed. The reactivity of some shale samples pyrolyzed in the TG apparatus and directly gasified without cooling is also displayed in Figure 10. In these runs an activation energy in the same order as that of the fluidized bed is found. However, the reactivity is higher than in the fluidized bed, but lower than those of the prepyrolyzed chars.

The observed difference in reactivity can be discussed in terms of the pretreatment of the char, where the heating rate and the final pyrolyzing temperature of the shale are of importance. From Figure 10 it can be stated that the lower the heating rate and the lower the pyrolyzing temperature the more reactive is the resulting char.

In the fluidized bed the heating rate of a newly introduced particle is high. The particles used ranged from 0.2 - 2 mm. Depending on the particle size, the heating rate calculated from Carslaw and Jaeger (1959) can be between 500 - 5000 K/s. In the TG runs the shale has been pyrolyzed with the maximum rate of 20 K/s, while the prepyrolyzed chars were heated at 0.5 K/s. In Figure 10 the reactivity of the char samples (a) to (e) clearly demonstrates the effect of the pyrolyzing temperature. Part of the reactivity differences observed can be explained by the variation in BET area. Sample (a) which was heated to 500 °C has a four times larger area than sample (e) which was pyrolyzed at 850 °C.

Furthermore, a higher hydrogen content in the samples pyrolyzed at the lower temperatures can be expected to increase the reactivity. It should be noted that the residual effects of volatilization are excluded from the reaction rates for the low temperature pyrolyzed chars. The rates are measured after 10 - 25 minutes of reaction time in the steam atmosphere. Thus the low temperature pyrolysis appears to leave a structure richer in residual hydrogen and thereby less graphitized and with higher BET areas than that of the fluidized bed. In the fluidized bed, BET areas between 15 and 25 m²/g were measured.

Several shale and char samples from both the TG and the fluidized bed runs have been examined in a SEM. In the magnification range 3000 - 30 000 times, no conclusive differences could be observed between the samples.

The results reported here are contradictory to those found by Burnham (1979) in his investigation on Colorado shale. It was shown that a rapid heating rate increases the reactivity, while during a slow heating the micropores are plugged and catalytic activity from the ash is retarded by coking of tar and oil. This is more probable in the case of Colorado shale with its high oil yield, than for Ranstad shale which only gives 1.5 - 2 wt % of the shale or 8 - 10 % of the kerogen as oil.

In investigations on coal volatilization, reported by Howard and Anthony (1976) in their review of pyrolysis work, it is concluded that a rapid heating generates more volatiles than a slow heating which also could imply a lower residual hydrogen content of the char.

In summary, it can thus be concluded that the char reactivity is quite dependent on the conditions of volatilization of the shale, e.g. heating rate and final temperature level. Additionally, the lower reactivity of the fluidized bed, shown in Figures 10 and 11, can be an effect of product gas retardation, although the carbon monoxide and hydrogen partial pressures in the reactor are low, due to the large steam and carbon dioxide flows used.

The retarding effect of carbon monoxide and hydrogen can be shown to have a marked influence also for the conditions in the fluidized bed. The contents of carbon monoxide and hydrogen in the wet gas, by steam gasification are in the order of 0.5 to a few percent. A calculation of the fluidized bed reactivity using the TG-kinetic data and the experimental wet gas analyses indicated a reactivity close to the measured rates in the range 800 to 850 °C.

A complete consistency is not to be expected since, as pointed out above, the volatilization conditions are quite different in the two systems.

4. CONCLUSIONS

In the investigation described, it has been shown that the rate of gasification of the shale char in the presence of steam, hydrogen, carbon dioxide and carbon monoxide can be expressed by a modified Langmuir-Hinshelwood equation.

Similarly to coal a strong retardation effect of hydrogen and carbon monoxide on the reaction rate was observed. The effect was linear in partial pressure of hydrogen while the retardation by carbon monoxide showed very weak partial pressure dependence with an exponent of 0.05 in carbon dioxide atmosphere and 0.25 in steam.

The pyrolyzing conditions of the shale were of importance to the reactivity of the residual carbon in the char. A slow heat rate and a low final pyrolysis temperature was shown to yield a more hydrogen rich char with higher gasification reactivity than the flash pyrolysis conditions of the fluidized bed runs.

The adding of potassium and calcium salts to the char gave only a minor increase of the gasification rate.

ACKNOWLEDGMENT

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NOTATION

c_C	= carbon concentration in the char, (mole C/kg char)
E_A	= activation energy, (kJ/mole)
k_0	= preexponential factor in Arrhenius equation, (s^{-1}) or (Pa^{-1})
k^{I-III}	= first order rate constants for the FeS reactions with H_2O , CO_2 and H_2 , (s^{-1})
k_{1-6}	= constants in the Langmuir-Hinshelwood expressions (17) and (18), (s^{-1}) or (Pa^{-1})
p_i	= partial pressure of component i, (Pa)
t	= time
T	= absolute temperature, (K)
r_C	= reaction rate of carbon, (mole C/kg char, s)
W_0	= initial sample weight
W	= actual weight of char sample
W_{ash}	= weight of ash in the char sample
W_C	= actual carbon weight
W_O	= actual oxygen weight (in FeO)
W_{oS}	= initial sulphur weight
W_S	= actual sulphur weight

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TABLE 1

Shale and Char Analysis

Item	Shale (wt %)	Char (wt %)
Moisture	5.0	-
Volatile matter ⁺	13.0	-
Fixed carbon ⁺	12.1	-
Ash ⁺	74.9	82.5
% C	15.0	12.9
% H	1.4	0.2
% N	0.4	0.1
% O	1.7	-
% S	7.0 ⁺⁺	4.3

+ moisture free

++ 5.2 % pyritic, 1.8 % organic

TABLE 2

Kinetic Parameters for the Reactions of FeS with H₂O, CO₂ and H₂.

Reaction	Preexponential factor (s ⁻¹)	Apparent Activation Energy (kJ/mole S)
FeS + H ₂ O	1.0·10 ⁻⁴	70
FeS + CO ₂	31.0	130
FeS + H ₂	9.0·10 ⁻²	72

TABLE 3

Kinetic Parameters for the Steam and Carbon Dioxide Gasification of Ranstad Shale Char.

Steam Gasification				
$-r_C = k_1 \cdot \frac{k_2 \cdot p_{H_2O}}{1 + k_2 \cdot p_{H_2O} + k_3 \cdot p_{H_2} + k_3' \cdot p_{CO}^{0.25}} \cdot c_C \quad (\text{mole C/kg char, s})$				
Constant	Preexponential factor (s ⁻¹)	Apparent Activation Energy (kJ/mole C)	Preexponential factor (Pa ⁻¹) ^α	Apparent Activation Energy (kJ/mole C)
k ₁	1.0 · 10 ¹⁶	404	-	-
k ₂	-	-	2.7 · 10 ⁻¹⁴	-188
k ₃	-	-	1.3 · 10 ⁻¹⁰	-144
k ₃ '	-	-	0.5	-10
Carbon Dioxide Gasification				
$-r_C = k_4 \cdot \frac{k_5 \cdot p_{CO_2}}{1 + k_5 \cdot p_{CO_2} + k_6 \cdot p_{CO}^{0.05} + k_6' \cdot p_{H_2}} \cdot c_C \quad (\text{mole C/kg char, s})$				
k ₄	9.6 · 10 ⁹	301	-	-
k ₅	-	-	3.4 · 10 ⁻⁸	-65
k ₆	-	-	1.1 · 10 ⁻⁴	-126
k ₆ '	-	-	9.4 · 10 ⁻⁸	-94

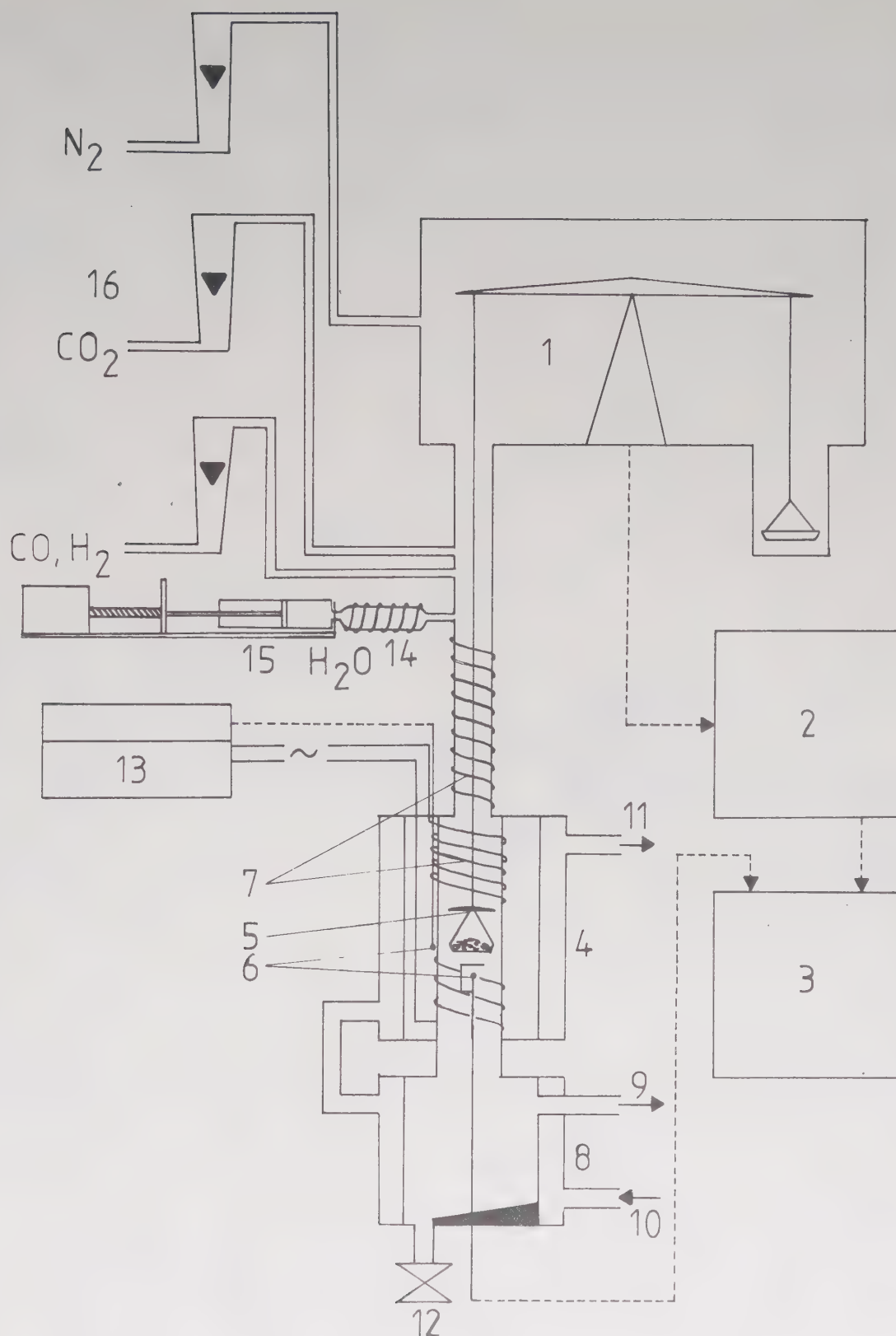


Figure 1

Thermogravimetric apparatus.

- | | |
|-------------------------------|-------------------------------|
| 1. Microbalance, weight unit | 2. Microbalance, control unit |
| 3. Two channel strip recorder | 4. Furnace |
| 5. Sample basket | 6. Thermocouples |
| 7. Heating coils | 8. Condenser |
| 9. Gas outlet | 10. Cooling water inlet |
| 11. Cooling water outlet | 12. Condensate outlet |
| 13. Temperature controller | 14. Steam vaporizer |
| 15. Step motor driven syringe | 16. Rotameters |

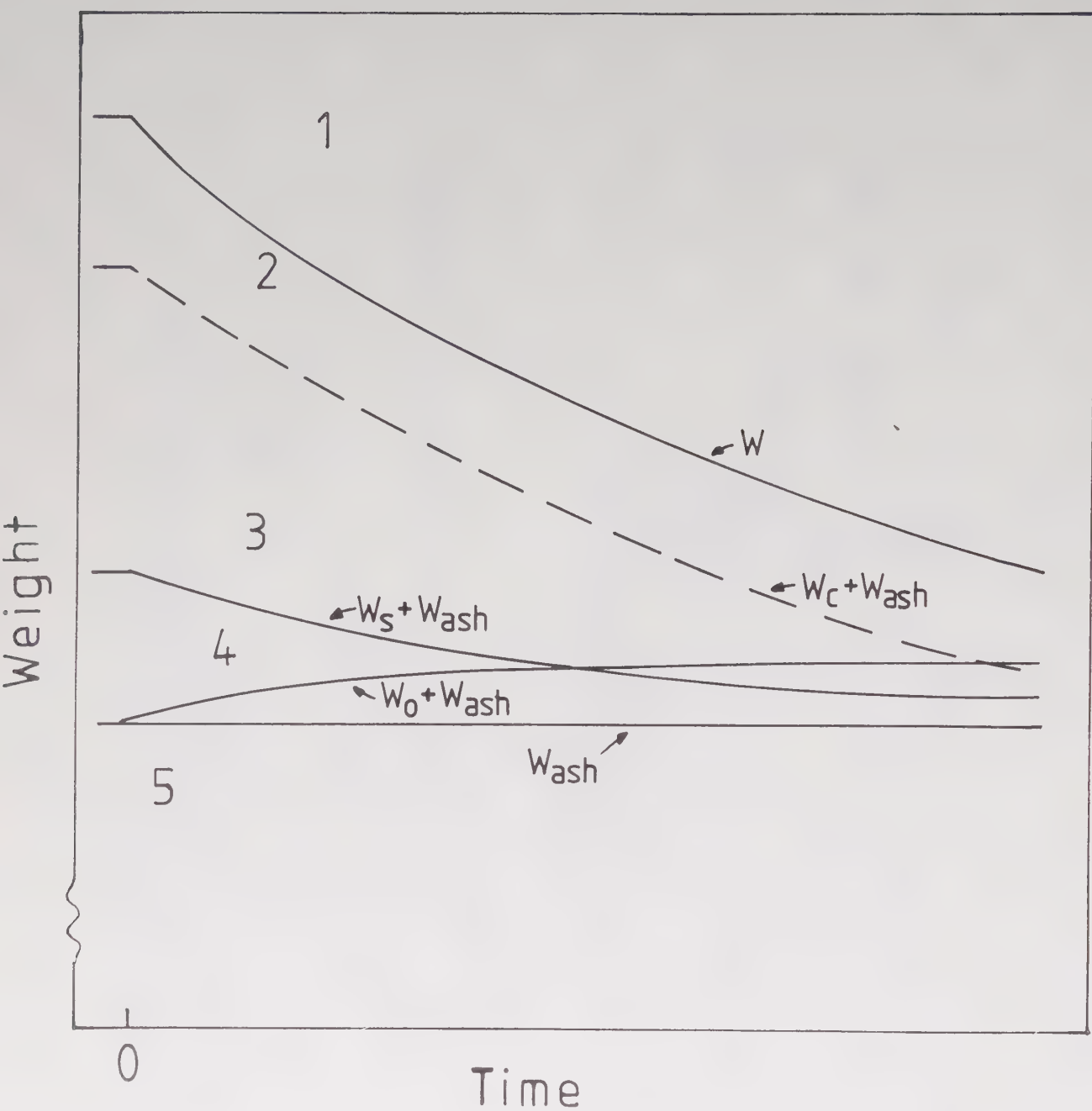


Figure 2

Schematic weight loss curves in H_2O , CO_2 and H_2 atmosphere.

Line 1. Observed weight

Line 2. Weight of carbon + ash $W_C + W_{\text{ash}}$

Line 3. Weight of sulfur + ash $W_S + W_{\text{ash}}$

Line 4. Weight of Oxygen due to FeO formation $W_O + W_{\text{ash}}$

Line 5. Ash weight of the sample W_{ash}

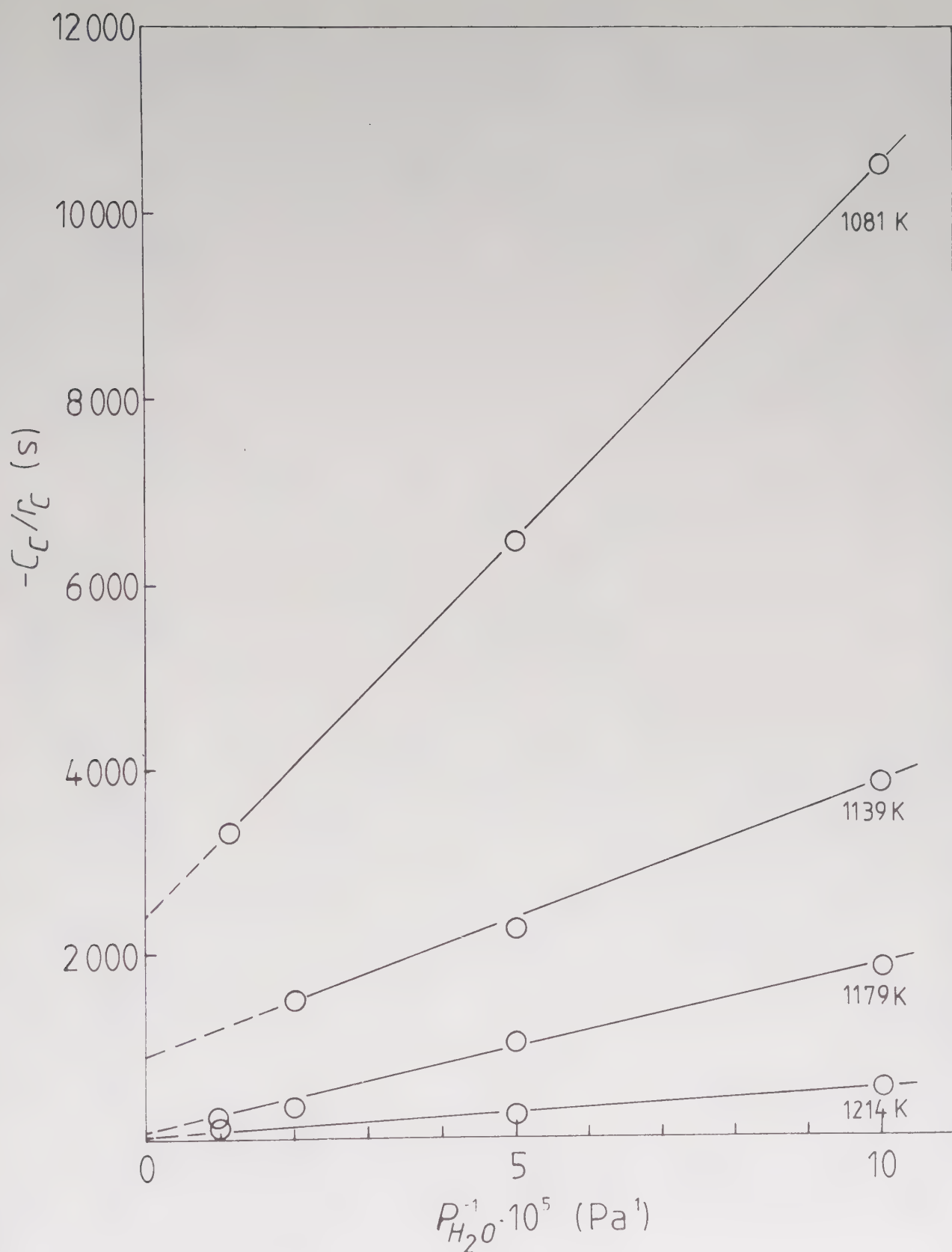


Figure 3

Gasification in steam-nitrogen atmosphere,

$-c_c/r_c$ (second) vs. $1/p_{H_2O}$ (pascal⁻¹). Parameter: Temperature

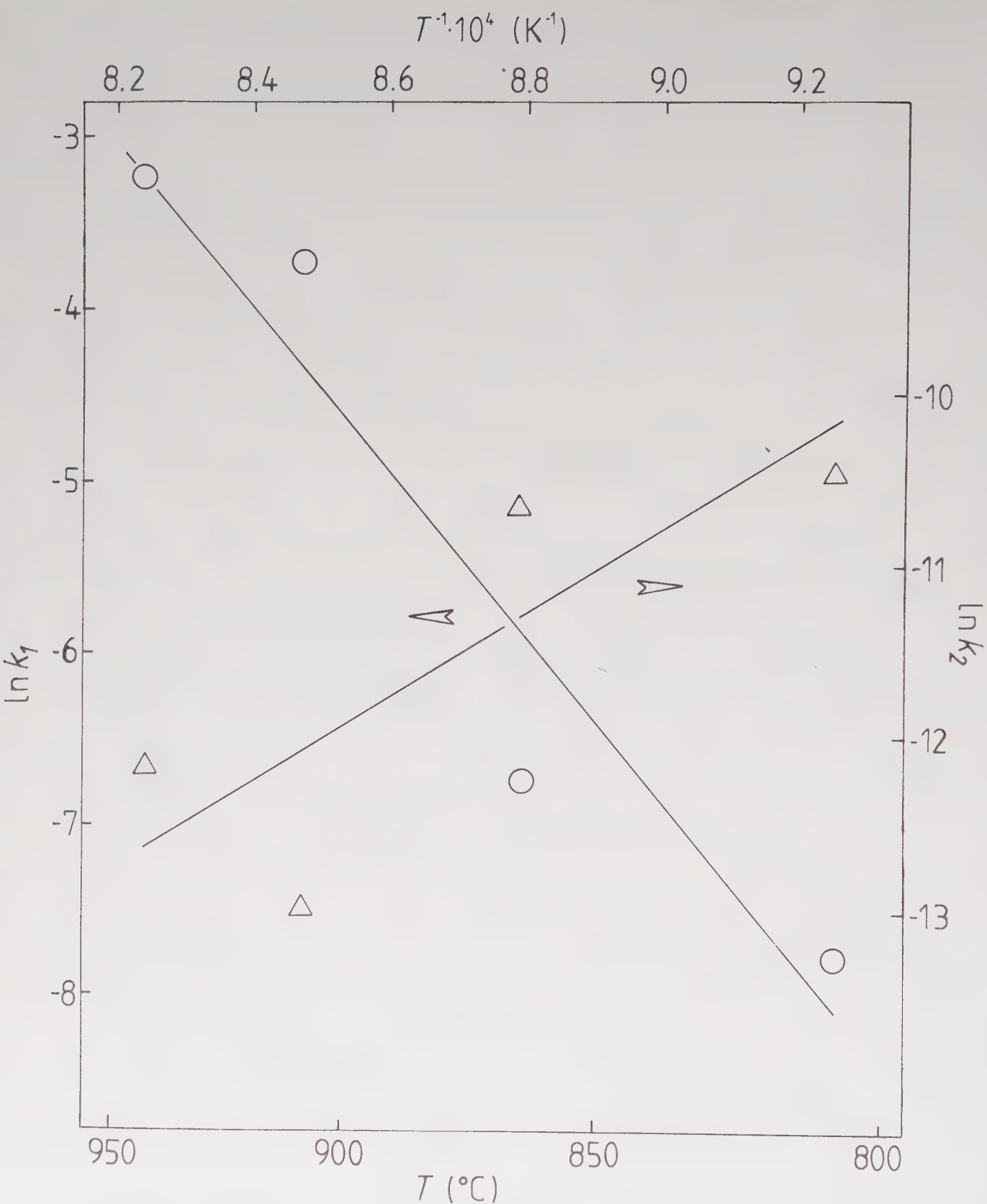


Figure 4

Arrhenius plot, steam-nitrogen atmosphere,

$\ln k_1$, $\ln k_2$ vs. $1/T \text{ (K}^{-1}\text{)}$. Base: k_1 (second), k_2 (pascal)

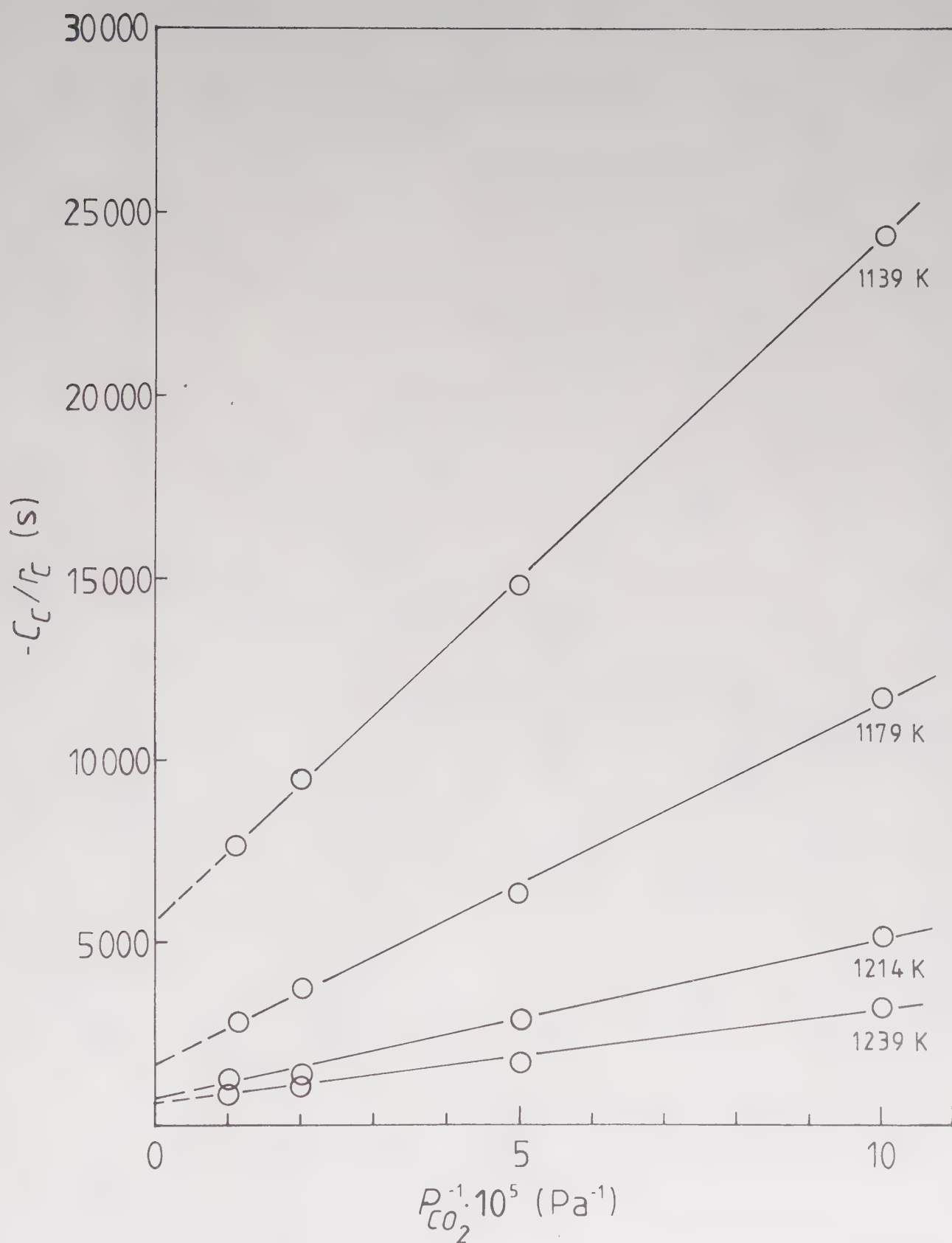


Figure 5

Gasification in carbon dioxide-nitrogen atmosphere,
 $-c_c/r_c$ (second) vs. $1/p_{CO_2}$ (pascal⁻¹). Parameter: Temperature

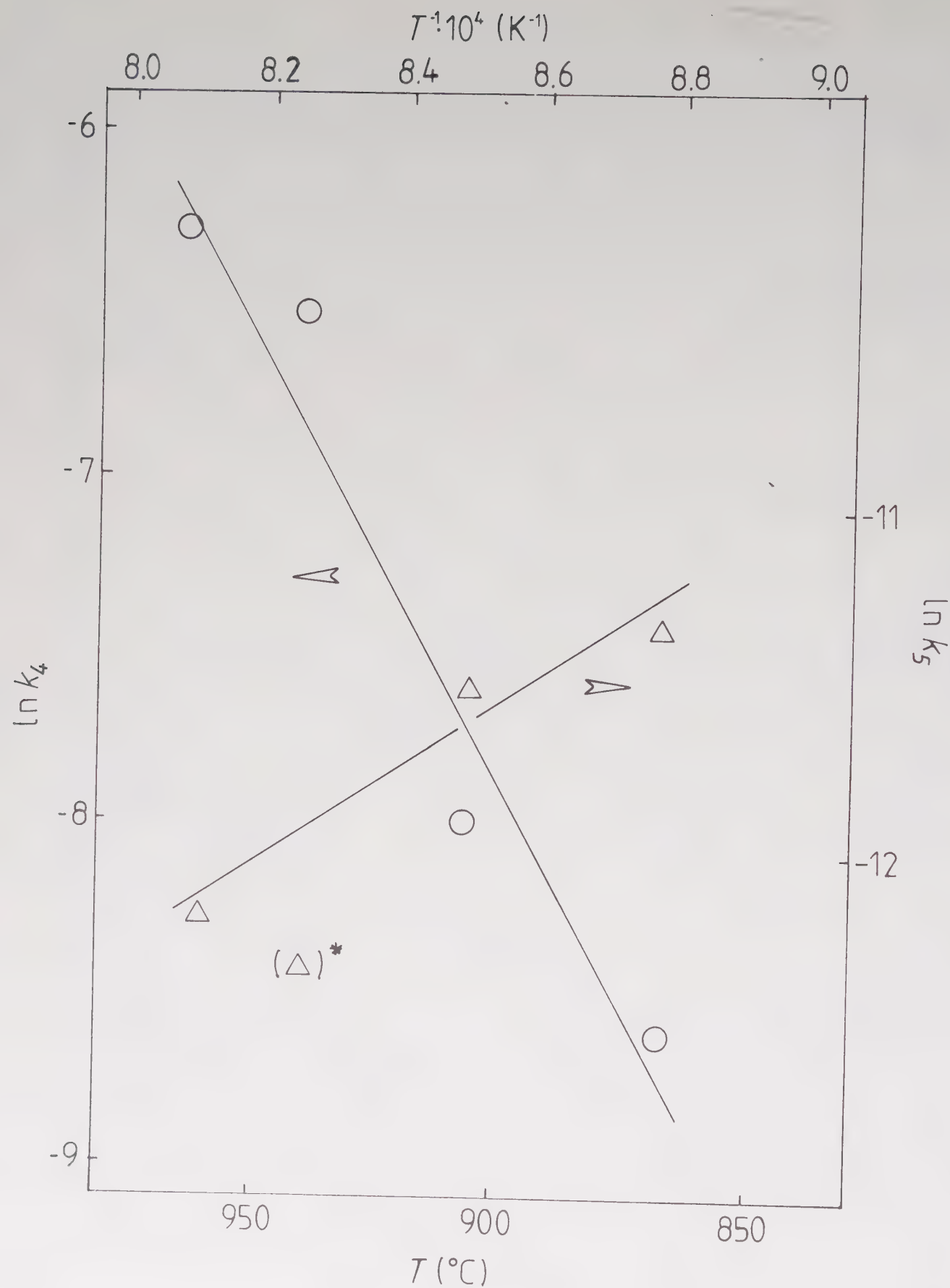


Figure 6

Arrhenius plot, carbon dioxide-nitrogen atmosphere, $\ln k_4$, $\ln k_5$ vs. $1/T \text{ (K}^{-1}\text{)}$. Base: k_4 (second), k_5 (pascal).

*Data point, excluded from least square fitting.

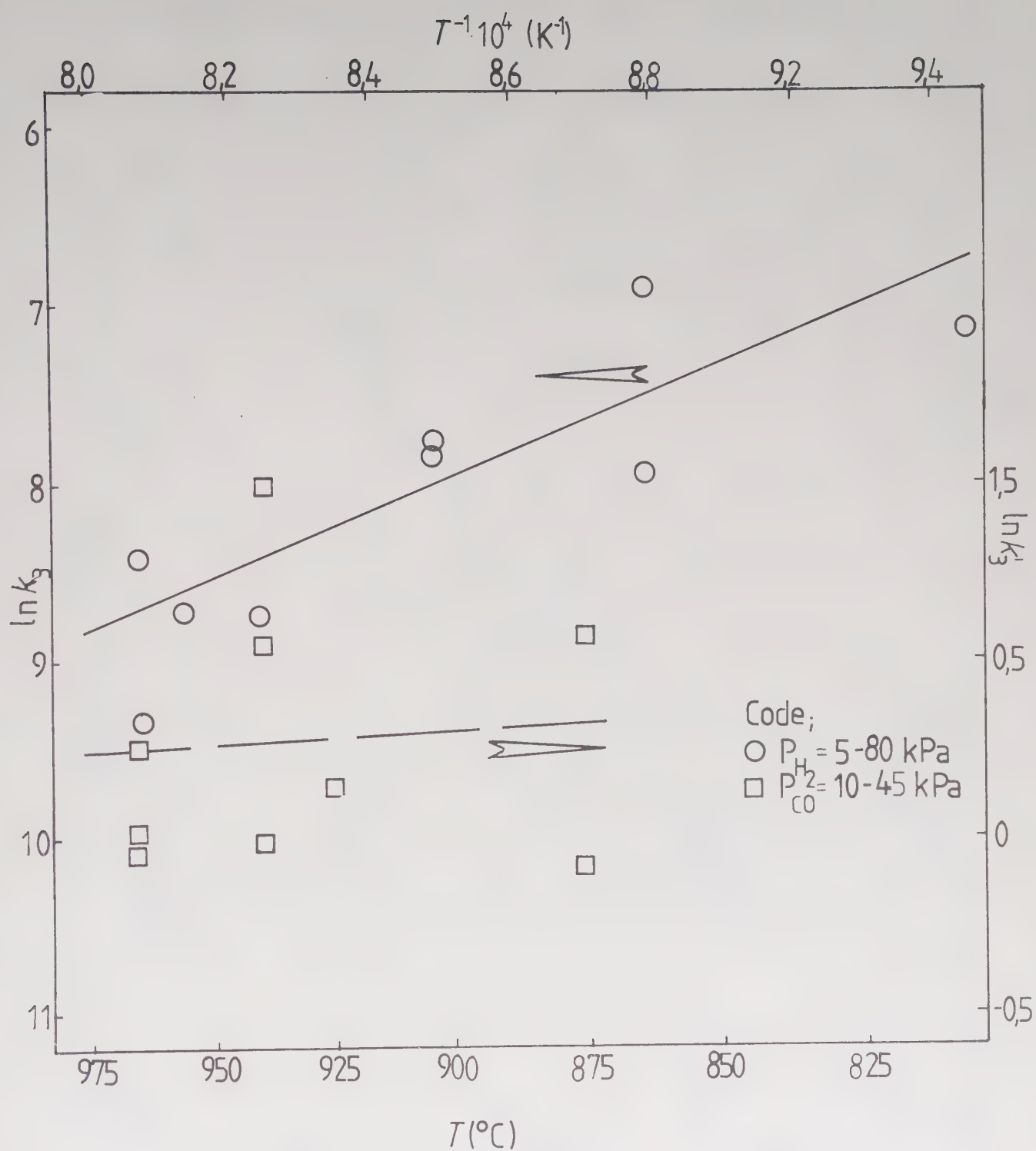


Figure 7

Arrhenius plot, steam-hydrogen and steam-carbon monoxide
 monoxides

$\ln k_3, \ln k'_3$ vs. $1/T \text{ (K}^{-1}\text{)}$. Base: $k_3, k'_3 \text{ (pascal)}^\alpha$

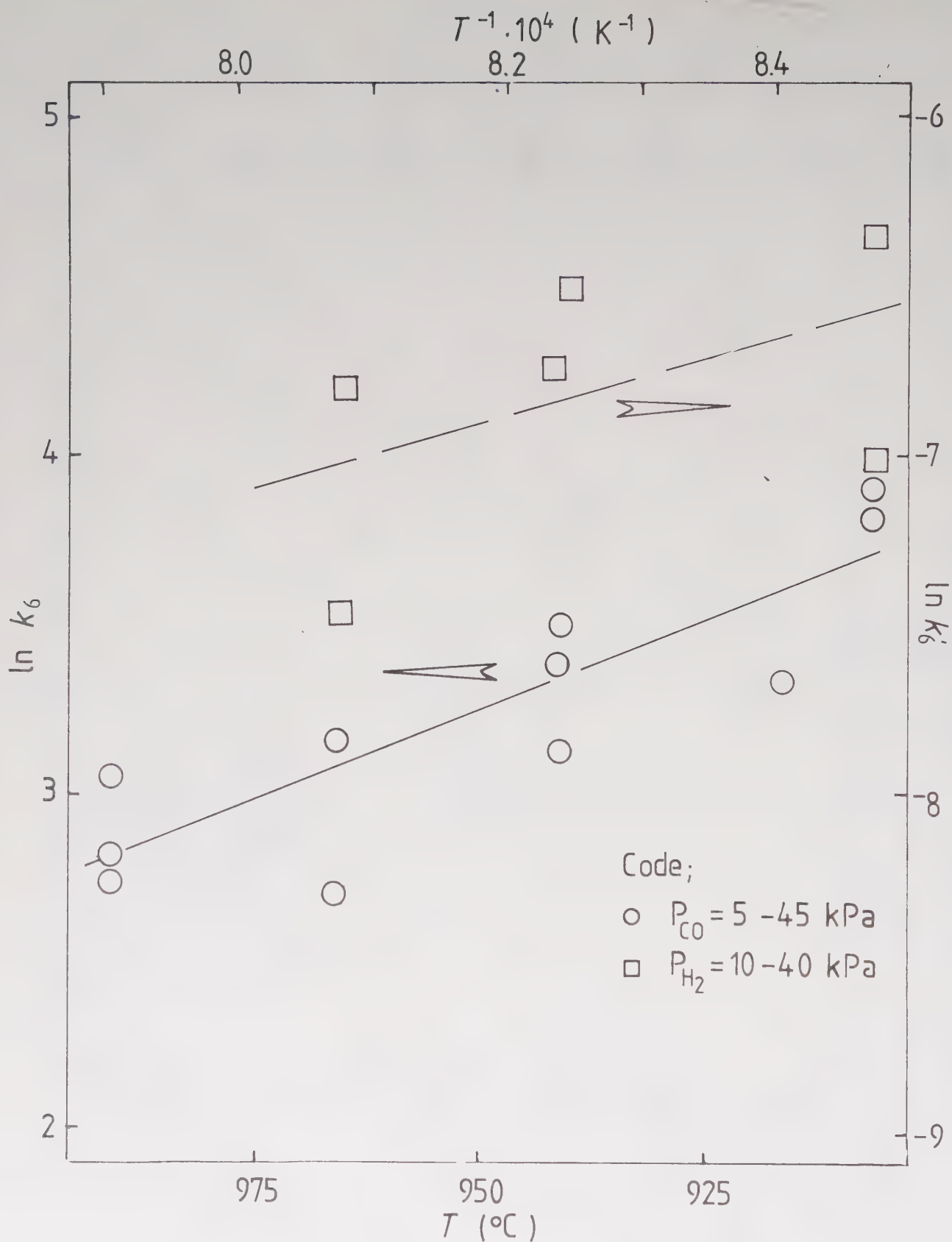


Figure 8

Arrhenius plot, carbon dioxide-carbon monoxide and carbon dioxide-hydrogen atmospheres

$\ln k_6, \ln k'_6$ vs. $1/T (\text{K}^{-1})$. Base: k_6, k'_6 (pascal) ^{α}

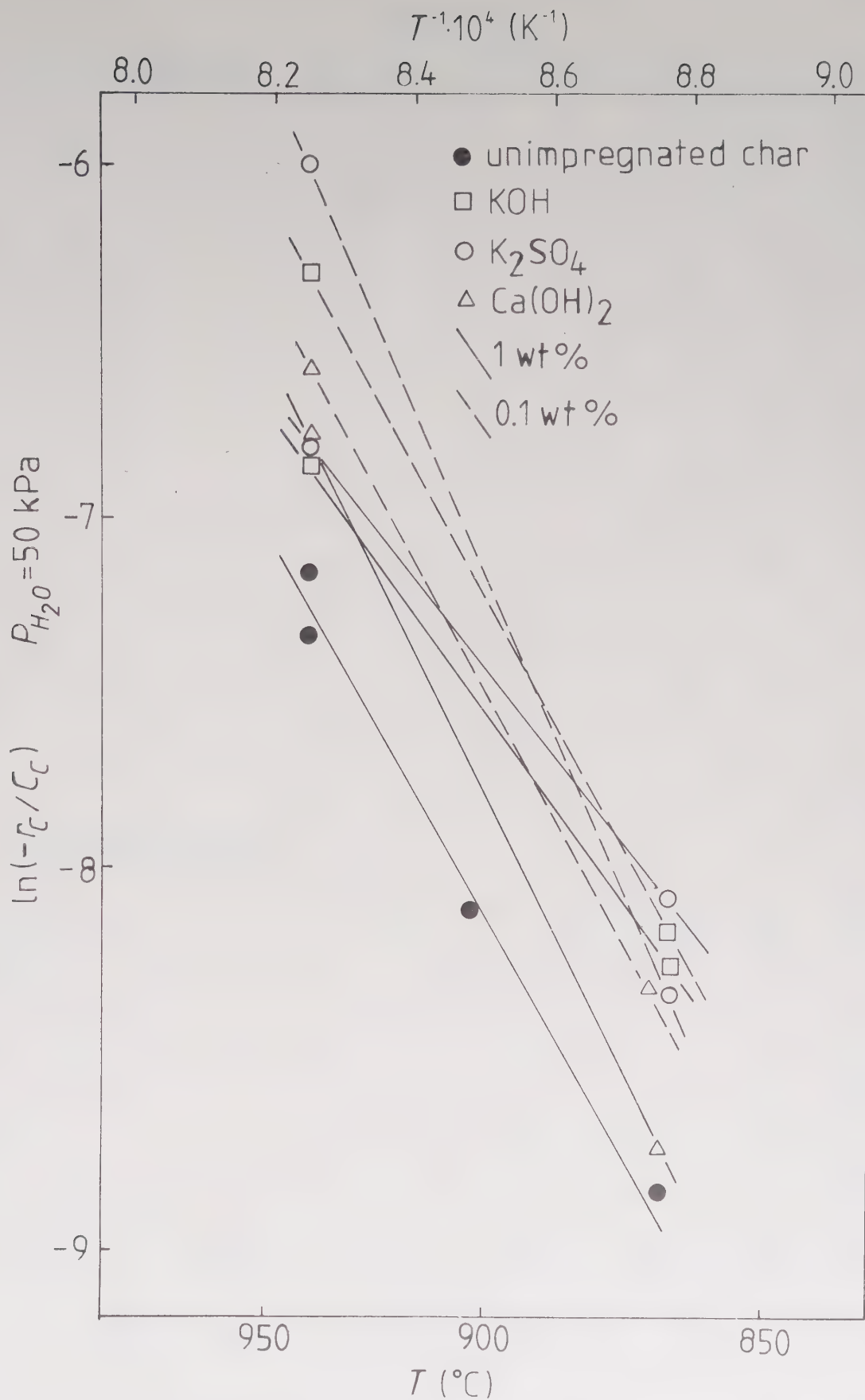


Figure 9

Impregnation of shale char with KOH, K_2SO_4 and $Ca(OH)_2$, 0.1 and 1 wt-%. Arrhenius plot $\ln(-r_c/c_c)$ vs. $1/T \text{ (K}^{-1}\text{)}$

Base: (second)

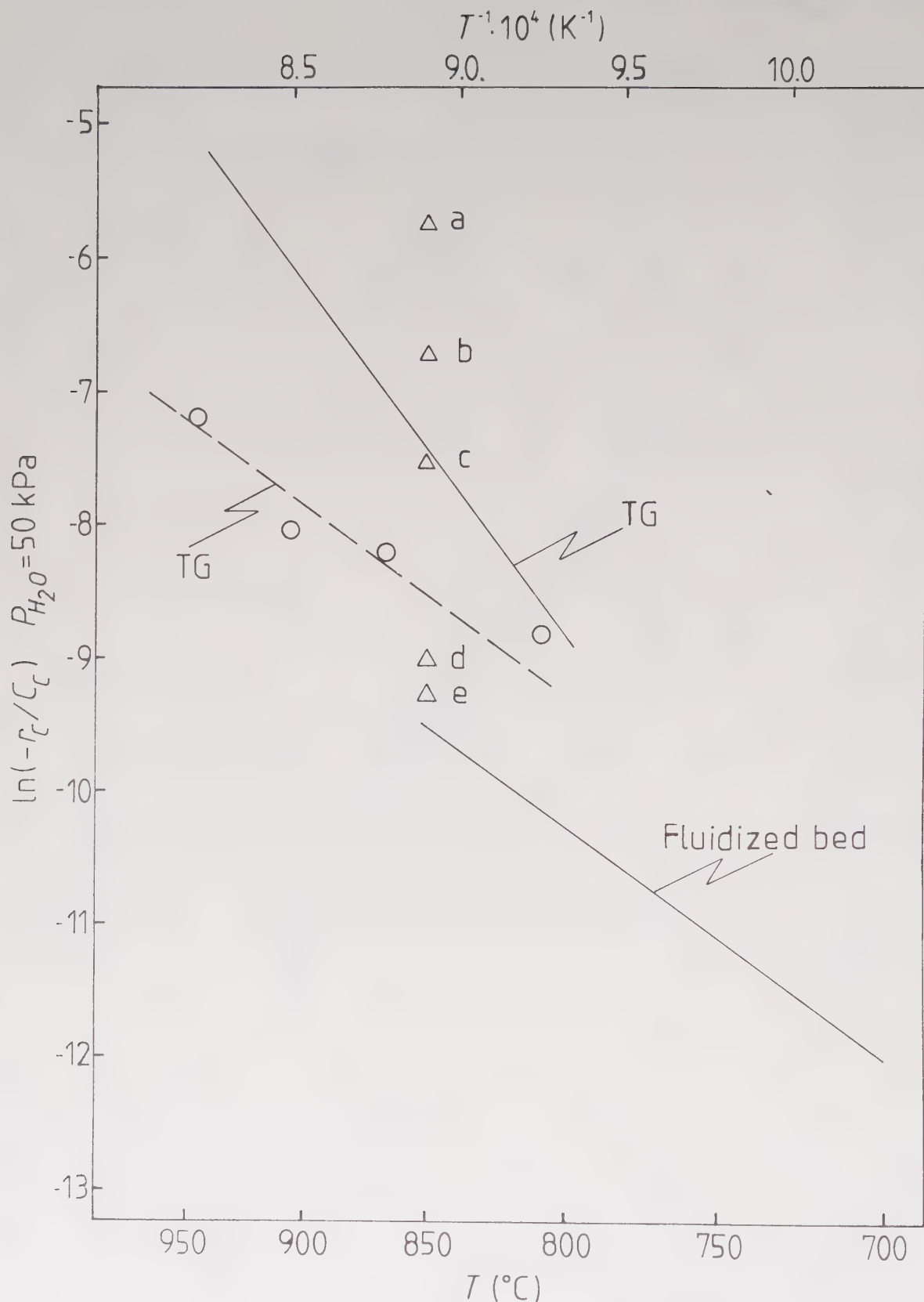


Figure 10

Comparison, TG and Fluidized bed reaction rates, steam atmosphere, $P_{H_2O} = 50 \text{ kPa}$. Base: (second).

TG solid line, char sample (c).

TG dashed line, raw shale, heating rate 20 K/s.

Fluidized bed, raw shale, calc. heating rate; $\geq 500\text{--}5000 \text{ K/s}$,

BET area of fluidized bed chars; $15\text{--}25 \text{ m}^2/\text{g}$.

Key to figure:

Char sample	Pyrolysis conditions			Char analysis		
	Temp (K)	Time (h)	Heating rate (K/s)	% C	% H	BET ₂ area (m ² /g)
a	773	3	0.5	13.2	0.45	51
b	973	1	0.5	13.0	0.25	36
c	973	3	0.5	12.9	0.20	40
d	1123	1	0.5	12.9	0.17	19
e	1123	6	0.5	11.2	0.13	14

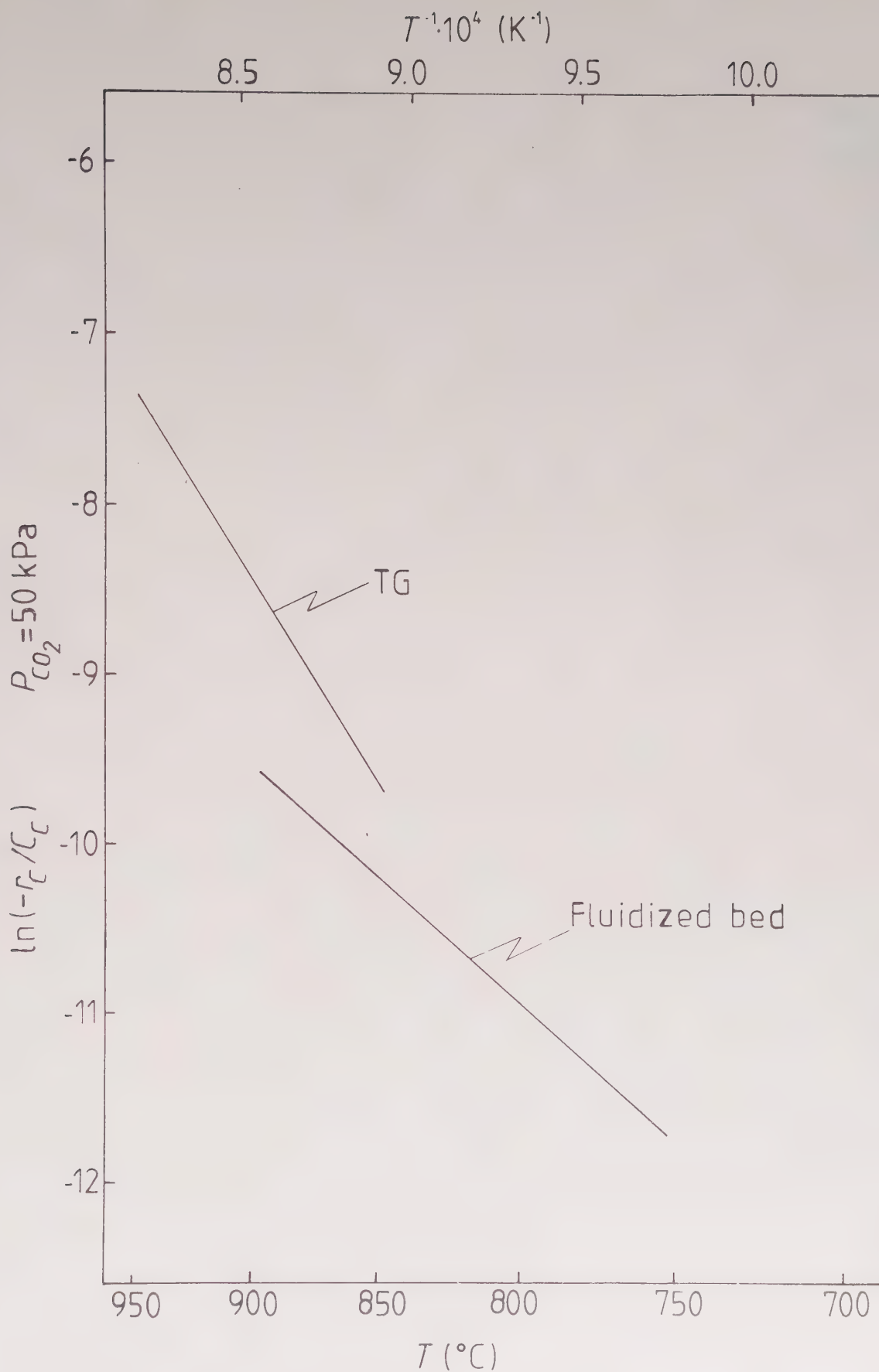


Figure 11

Comparison, TG and Fluidized bed reaction rates, carbon dioxide atmosphere, $p_{CO_2} = 50 \text{ kPa}$. Base: (second)

A KINETIC STUDY OF THE HETEROGENEOUS SHIFT REACTION
OVER SHALE CHAR AND KEROGENFREE ASH.

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ABSTRACT

The kinetics of the shift reaction, $\text{CO} + \text{H}_2\text{O} \rightleftharpoons \text{CO}_2 + \text{H}_2$ have been investigated over a bed of shale char and kerogen free ash in the temperature range between 650 and 800 °C.

The experiments were carried out in a differential reactor, and the reaction rates were described by power law equations but could also be fitted to a Langmuir-Hinshelwood type expression at 800 °C.

The reaction rate over shale char was slightly exceeding that of kerogen free ash. Compared with the fixed carbon reactions, the shift reaction is between one and two magnitudes faster.

1. INTRODUCTION

The interest of studying the shift reaction, in connection with fixed carbon gasification, is assigned to a number of reasons.

At atmospheric pressure the reaction system of carbon gasification will be described by the reactions;

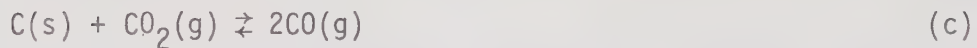
Water gas reaction;



Shift reaction;

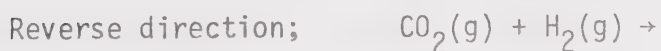


Boudouard reaction;



From above it can be stated that knowledge of the shift reaction kinetics is necessary for a prediction of the ultimate gas composition from the gasifier. Additionally, in calculating the steam decomposition, kinetics of the shift reaction must be known. The shift reaction occurs both as a heterogeneous gas/solid catalyzed reaction and as a homogeneous gas phase reaction, the rate of the latter is however negligible at temperatures below 1000 °C as pointed out by the references (4) and (5).

In the following the terms forward and reverse direction of the shift reaction will be used, defined as;



2. APPARATUS AND EXPERIMENTAL

The experiments have been conducted in a fixed bed reactor, operated as a differential unit. The experimental set-up is displayed in the Figures 1 a,b. Figure 1 a shows the apparatus when running with non-condensable gases. In Figure 1 b the steam vaporizer used for runs with steam is shown. The vaporizer has a maximum capacity of about $2 \cdot 10^{-3}$ moles/s of superheated steam, the flow rate is controlled by the peristaltic pump, also shown in the figure.

Inlet gases, CO, CO₂, H₂ and N₂ were measured by rotameters calibrated for the pressure drop of the reactor system, 2 kPa. The gases are mixed in a packed column before being preheated in an empty quartz tube of the same type as the reactor.

The reactor consists of a 0.35 m long vertical quartz tube with an inner diameter of 34 mm. The catalyst bed, the shale char or the ash, is placed on a sintered quartz plate situated 25 cm from the top of the tube.

The temperature in the bed is measured by a thermocouple inserted into a thin quartz tube. A second thermocouple is placed on the outside wall of the reactor to indicate radial temperature gradients.

Before being pumped to analysis, the gas is cooled, water is tapped and measured. The gas chromatography system used for the gas analysis has been described elsewhere (1).

The reaction rate was related to a strictly measured nitrogen flow (Figure 1 a) used both as internal standard and as dilutant.

In the runs, a sample of 6 g of shale char or kerogenfree ash was placed in the reactor, which was then, under nitrogen atmosphere, heated to the required temperature. After reaching the reaction temperature, the reactant gases were introduced and the reaction rate of the limiting component was determined from the gas analysis. The operation conditions were chosen in a way that the conversion of the limiting

gas component never exceeded 20 % of the calculated equilibrium conversion. The catalyst bed can therefore be considered as a differential unit and the general tube reactor expression;

$$\frac{dx_i}{dW} = - \frac{r_i}{(F_i)_{in}} \quad (1)$$

can be approximated with a difference equation;

$$\frac{\Delta x_i}{\Delta W} = - \frac{(r_i)_{ave}}{(F_i)_{in}} \quad (2)$$

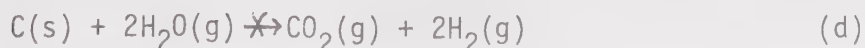
where

$$(r_i)_{ave} = \frac{(F_i)_{in} - (F_i)_{out}}{W} \quad (3)$$

3. RESULTS

The rate, and the occurrence of the shift reaction in connection with coal gasification have been studied by a number of investigators, (2, 3, 4, 5, 6).

Gadsby et al. (2), Johnstone et al. (3), conclude the approach of equilibrium conditions for the shift reaction over a carbonaceous surface. Hauk (6) presented kinetic data for the shift reaction indicating this reaction being much faster than the fixed carbon reactions. Hedden and Löwe (5) concluded that the shift reaction did not occur over their very pure reactor graphite. Wicke and Rossberg (4) proposed the shift reaction to be a subsequent step to the fixed carbon reactions, thus the reaction yielding carbon dioxide directly;



is not likely to occur.

In the production of ammonia and methanol, the shift conversion is an important process step and extensive studies of the kinetics over

commercial catalysts have been published (7, 8, 9, 10, 11). The early types of these catalysts used iron oxide as the active component, a specie which can be expected to be active also in the reaction over kerogen and sulphurfree shale ash.

The reaction rates for the forward and backward direction of the reaction have been studied separately by the initial rate method. Thus, the reactor was fed with binary mixtures of H_2O/CO and CO_2/H_2 . The partial pressure of the limiting gas component was varied in the range 0 to 40 kPa, keeping the other constant at 60 kPa by dilution with nitrogen to a total gas flow of $2.5 \cdot 10^{-3}$ moles/s.

With the assumption that the adsorbition of the reactants follow the Langmuir isotherm, the reaction rate, exemplified by the forward reaction, can be written;

$$-r = \frac{k_1 \cdot P_{H_2O} \cdot P_{CO}}{1 + K_{H_2O} P_{H_2O} + K_{CO} P_{CO}} \quad (4)$$

By letting the effect of the dominator be described by exponents on the partial pressures, the power law expression is obtained;

$$-r = k_2 \cdot P_{H_2O}^\alpha \cdot P_{CO}^\beta \quad (5)$$

In this expression no account is taken to the retarding influence of the reaction products and the validity of the equation is limited to partial pressures far from equilibrium.

By combining the forward and reverse reactions a general equation, having validity also at equilibrium, is obtained;

$$-r = \frac{k_3 P_{H_2O} P_{CO} - k_4 P_{H_2} P_{CO_2}}{1 + K_{H_2O} P_{H_2O} + K_{CO} P_{CO} + K_{CO_2} P_{CO_2} + K_{H_2} P_{H_2}} \quad (6)$$

which can be approximated by equation (7).

$$-r = k_5 P_{H_2O}^\alpha P_{CO}^\beta - k_6 P_{H_2}^\gamma P_{CO_2}^\delta \quad (7)$$

In equation (6) the constants will all have an Arrhenius type temperature dependence;

$$k_i = k_{i0} e^{-E_{Ai}/RT} \quad (8)$$

Due to this, the exponents in equation (7) will also be functions of temperature, but over limited temperature ranges, this dependence is usually neglected.

3.1 REACTION OVER SHALE CHAR.

The shale char used in the tests were obtained from the Ranstad Skifferaktiebolag and has been sampled from an oxygen blown pilot plant gasifier. An ultimate analysis is given in Table 1.

Before starting the proper test program, the selfcatalytic properties of the reactor and the influence of internal and external mass transfer were to be checked.

By feeding equimolar mixtures of CO_2 and H_2 to the empty reactor, only traces of CO and H_2O could be detected at 800°C , thus concluding the negligible extent of self catalyzis. To determine the influence of intra particle mass transfer, test runs were carried out with different particle sizes. No significant difference in reaction rate was found by using 0.25 and 1.8 mm in diameter particles at 800°C . The absence of a gas film resistance with the gas velocities to be used was stated by plotting the conversion of the limiting gas component against the total gas flow, keeping the ratio catalyst weight to total gas flow constant. Hence, the chemical reaction control could be concluded at 800°C .

Before evaluating the reaction rate from the gas analysis, the rate has to be corrected for the influence of the fixed carbon reactions (a) and (c).

The magnitude of these reactions in comparison with the shift reaction was determined in two different ways. Firstly, the reaction rate of the watergas and the Boudouard reaction was calculated from the data obtained by Bjerle et al. 1980 (12).

Due to the strong retardation of both CO and H₂, and the quite low reaction rates for the water gas and the Boudouard reaction also without product gas retardation at temperatures below or equal to 800 °C, the contributions from these reactions were found to be only a few per cent of the reaction rate observed.

Secondly, the difference in reaction rate when alternating the gas atmosphere between CO₂+H₂ and CO₂ only, clearly demonstrated the negligible contribution from the fixed carbon reactions. Therefore, no correction of the rates calculated from the gas analysis were made.

Tests with variable partial pressures of H₂O/CO and H₂/CO₂ were conducted at 700 °C and 800 °C. Runs with one combination of partial pressures were carried out at 650 and 600 °C. At the latter temperature the reaction did not occur.

The apparent kinetic parameters obtained when fitting the experimental data to power law equations are given in the equations (9) and (10),

Forward direction;

$$-r_{CO} = 7.3 \cdot 10^{-4} e^{-55500/RT} P_{H_2O}^{0.2} P_{CO}^{0.6} \quad (\text{mole/kg char,s}) \quad (9)$$

Reverse direction;

$$-r_{CO_2} = 6.7 \cdot 10^{-8} e^{-52000/RT} P_{H_2}^{0.8} P_{CO_2}^{1.0} \quad (\text{mole/kg char,s}) \quad (10)$$

with the activation energy expressed in kJ/mole and the partial pressures in Pa. The variation of the partial pressure exponents between 700 °C and 800 °C were small, and the arithmetic mean values were used in the Arrhenius plots of Figures 2 and 3.

From the data the very weak dependence of the steam partial pressure can be stated.

In judging this, it is to be pointed out that the data obtained with steam are in general less reliable than those with uncondensable gases, since difficulties in keeping stable conditions in the vaporizer plagued the tests.

By least square fitting of the whole experimental matrix at 800 °C to a Langmuir-Hinshelwood expression the following parameters were obtained;

$$r = \frac{0.22 \cdot 10^{-10} (P_{H_2O} P_{CO} - 1.25 P_{H_2} P_{CO_2})}{1 + 10^{-5} (1.4 \cdot P_{H_2O} + 0.05 P_{CO} + 0.05 P_{CO_2} + 1.6 P_{H_2})} \quad (\text{mole/kgchar.s}) \quad (11)$$

A correlation of the experimental and the calculated reaction rates are displayed in Figure 4. The reaction rate is defined positive for the forward direction and the partial pressures are expressed in Pa. From this equation an equilibrium constant of 0.8 can be calculated which is in good agreement with the theoretical value of 1.02.

In Table 2 the reaction rate of equation (11) is compared with the one obtained by combining the equations (9) and (10) according to equation (12);

$$r_{\text{tot}} = (7.3 \cdot 10^{-4} e^{-6675/T} P_{H_2O}^{0.2} P_{CO}^{0.6} - 6.7 \cdot 10^{-8} e^{-6255/T} P_{H_2}^{0.8} P_{CO_2}^{1.0}) \quad (12)$$

The calculation showed that the two equations are consistent for partial pressures far from equilibrium or expressed in other terms, when the partial pressures of the product gases are small. Thus, the combined power law equation must be used with care for gas compositions approaching equilibrium.

3.2 REACTION OVER KEROGENFREE ASH

The catalytic properties of carbon and sulphurfree shale ash have been investigated by the initial rate method in similarity with the char case. The early types of commercial shift catalysts were usually based on iron oxide or iron oxide - chromium oxide, promoted with nickel, copper, molybdenum etc.

Temkin (13) and later Boreskov et al. (14) proposed the reaction mechanism of alternating oxidation and reduction of the iron surface. The iron content of kerogenfree ash is about 7.5 %, while chromium and nickel are present in trace amounts only, 0.04 and 0.025 % respectively. A certain catalytic activity due to the iron can thus be expected.

An extensive ash analysis is given in reference (12). The iron oxides are sensitive to sulphur compounds, and since the runs have been carried out with sulphurfree feed gas, a reduced activity of the ash can be expected when reacting the highly sulphur loaded product gas from the shale gasification. In shale char, the iron is inactively bound as sulphide, and the catalytic activity is due to other factors than the iron content.

The reverse reaction was studied by varying the partial pressures at 700 and 800 °C while the forward rate has been studied at 800 °C only. Below 650 °C the rate of reaction was negligible as also stated for the char.

The temperature dependence of the partial pressure exponents between 700 and 800 °C were found to be stronger for the ash than for the char. By using the arithmetic values being 0.44 for both the carbon dioxide and hydrogen exponents, apparent kinetic parameters could be obtained from Figure 5. Thus, the reverse rate over shale ash will be described by;

$$r_{\text{CO}_2} = - 2.6 \cdot 10^{-4} e^{-65300/RT} p_{\text{H}_2}^{0.44} p_{\text{CO}_2}^{0.44} \text{ (mole/kg char,s)} \quad (13)$$

with the activation energy expressed in kJ/mole and the partial pressures in Pa.

A comparison with the data obtained for the forward direction at 800 °C gave an experimental equilibrium constant of 3, compared with the theoretical value of 1.02.

3.3 EXPERIMENTAL REMARKS

In general, the runs with steam in the feed gas are more uncertain than those with uncondensable gases. Due to a chockwise vaporization constant steam partial pressures were very hard to achieve.

The temperature limit of 800 °C for both char and ash were due to sintering of the bed. Especially in the ash runs sintering could occur

after only 10 to 15 minutes of operation above 800 °C. Also for not melted ash the brick red colour of the original ash was converted to light grey and a rather strong ferromagnetism was stated. Thus, the Fe_2O_3 had converted to lower oxides or elemental iron. The reasons for the sintering are not clear. An x-ray investigation of the melted ash did not prove the existence of any iron oxides, but showed complex ferro-silicates. Therefore, it is likely that the reduced iron migrates into the silica matrix whereby low melting compounds are formed during the solid phase transformation.

4. DISCUSSION

The present study of the shift reaction has given some insight of the kinetic conditions over beds of shale char and carbonfree ash. Although the analysis has not been deep enough to allow a general kinetic model or an attempt to reaction mechanism, some conclusions of interest from an engineering point of view can be drawn.

The reaction rate over shale char was found to be a magnitude or more faster than over ash. It is very likely that the reaction mechanisms in the two cases are totally different. Over ash, it is possible, although in no way proven, that the iron content present as different oxides play a central role.

In the char, this can not be the case since the iron is inactively bound as iron sulphide. Here the catalytic properties are more likely to be related to the carbon structure. Firstly, the specific surfaces between char and ash differ by about a factor 10 which can in itself imply an increased reactivity. Secondly, it is shown by the fixed carbon gasification tests in (12) that the gasification rate is very strongly retarded by CO and H_2 . Since these compounds are fixed to the carbon surface in a chemisorbed state or as intermediate oxygen complexes their ability to react with a gaseous water or carbon dioxide molecule will be greater than on the surface of the shale ash.

If the reaction over ash does not involve the oxygen transfer by the iron, the reaction is likely to proceed by a simultaneous adsorption

of both reactants on adjacent sites which has a lower probability than a single molecule adsorption proposed in the char case.

When looking at the rate for the fixed carbon gasification in comparison with the shift rate, the shift reaction proceeds one to two magnitudes faster. Investigations in connection with coal gasification also indicate the fastness and the approach of equilibrium for the shift reaction (2, 3, 6).

Using the data from Hauk (6), the shift reaction over coal char exceeded the rate for the shale char at comparable conditions with a factor 5, whereas the steam - carbon reaction was about 10 times faster with the coal used by Hauk compared with shale.

Wicke and Rossberg (4) concluded the water gas and the shift reaction to proceed in series. If this is correct the watergas reaction is the rate controlling step in the system and, for a given combination of reaction parameters, the shift reaction can be assumed to approach equilibrium.

In gasification tests conducted in the bench scale fluidized bed, reported in (1), the occurrence of the shift reaction is clearly demonstrated. From Figure 6 it can be seen that by increasing the CO_2 partial pressure, the production of CO increases due to both the Boudouard and the shift reaction and, simultaneously, the hydrogen production detected in the gas analysis decreases.

Except in the fluidized bed itself, it is likely that the shift reaction proceeds above the bed level within the suspension of fine solids in the entrainment zone and in other parts of the reactor system where the temperature exceeds 600°C .

5. CONCLUSIONS

For the kinetics of the shift reaction over shale char and ash, the findings can be summarized as;

- The chemical reaction is the rate controlling step with the particle diameters (0.2 - 1.5 mm) and the superficial gas velocity (0.5 m/s) used.
- The reaction is considerably faster than the fixed carbon gasification rates, and by assuming the shift reaction being subsequent to the water gas reaction, conversions approaching equilibrium can be assumed for the shift reaction.
- The reaction rate is faster over shale char compared with carbon and sulphurfree ash.
- Fitting the data to initial rate power law expressions gave an equation having limited validity close to equilibrium, where a least square fitted Langmuir-Hinshelwood expression could better describe the reaction rate.

ACKNOWLEDGEMENT

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NOTATION

E_{Ai} = apparent activation energy, (kJ/mole)

F_i = molar flow of component i (mole/s)

k_{i0} = preexponential factor in Arrhenius equation

K_{H_2O} , K_{CO} , K_{CO_2} , K_{H_2} = Adsorption constants in the Langmuir-Hinshelwood equations (Pa^{-1})

p_i = partial pressure of component i, (Pa)

r_i = reaction rate of component i (mole/kg catalyst, s)

W = catalyst load (kg)

x_i = conversion of component i

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TABLE 1.

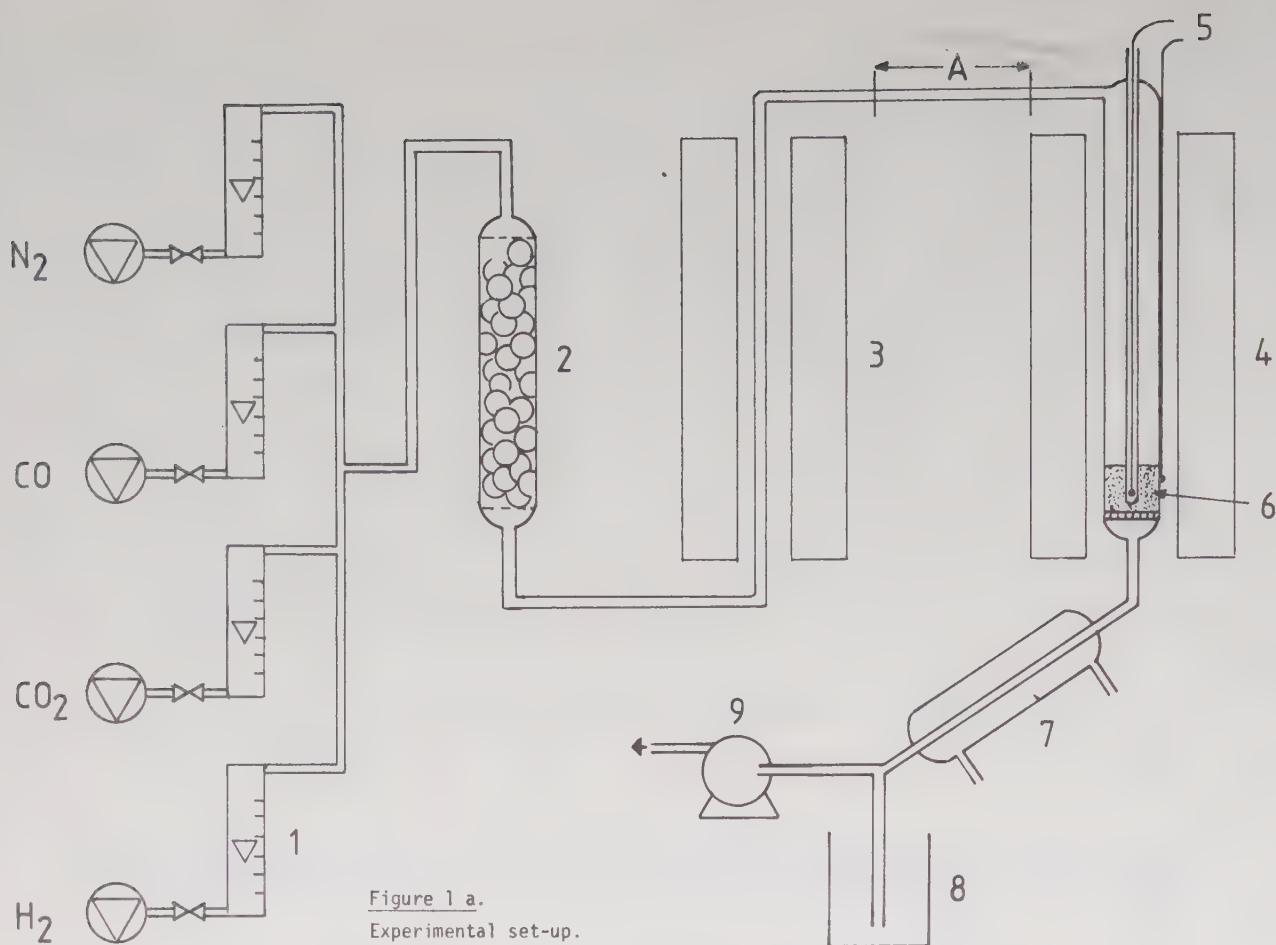
Steam gasified char from the Ranstad pilot plant gasifier used in the shift conversion study.

	wt %
% C	10.9
% H	0.2
% N	0.1
% S	4.3
Ash	85.5

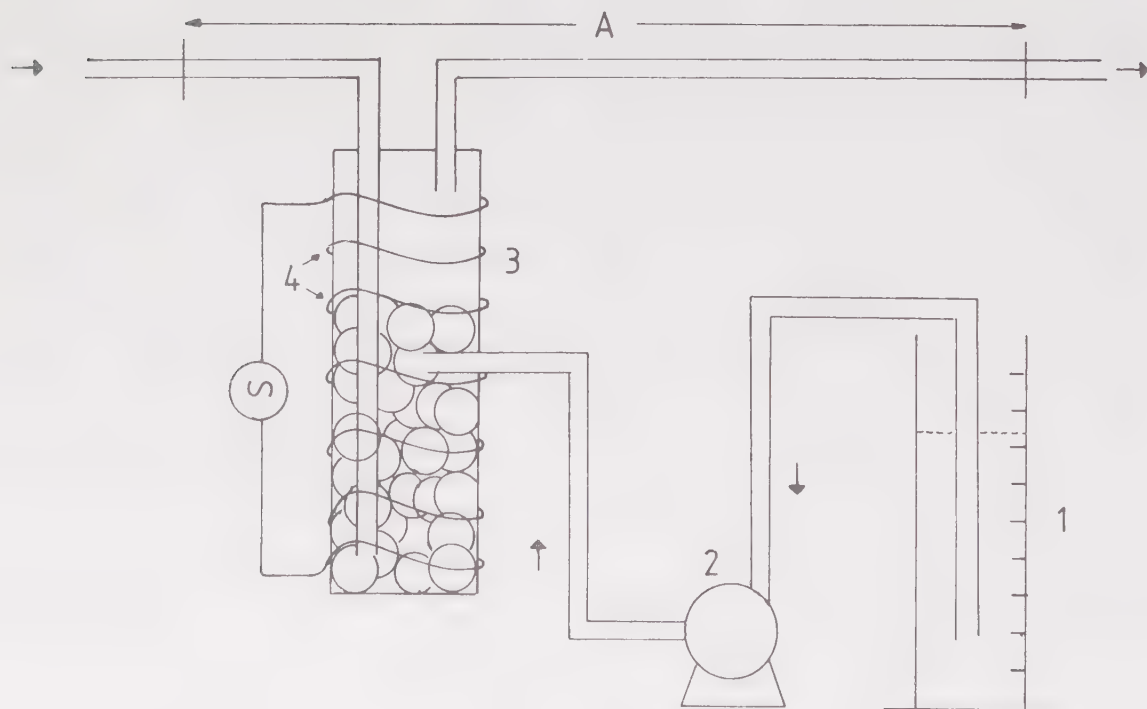
TABLE 2.

Comparison of the Langmuir-Hinshelwood and the power law rate equations at 800 °C. (forward rate defined positive)

Partial pressures (kPa)				Reaction rate mole/kg char,s	
H ₂ O	CO	H ₂	CO ₂	L-H eq.(11)	Power law eq.(12)
25	25	25	25	-0.0019	-0.0114
50	50	—	—	0.0319	0.00833
—	—	50	50	-0.0688	-0.0566
40	10	20	30	-0.00375	-0.000314
10	40	40	10	-0.00166	-0.0420
60	10	20	10	0.00382	0.00215
10	10	50	30	-0.0237	-0.0316
40	10	10	40	-0.000995	-0.00946



- | | |
|----------------------|--------------------|
| 1. Rotameters | 6. Char or ash bed |
| 2. Gas mixing column | 7. Gas cooler |
| 3. Gas preheater | 8. Water trap |
| 4. Reactor | 9. Gaspump |
| 5. Thermocouples | |



- | | |
|---------------------|----------------------|
| 1. Water byrette | 3. Vapourizer vessel |
| 2. Peristaltic pump | 4. Heating coils |

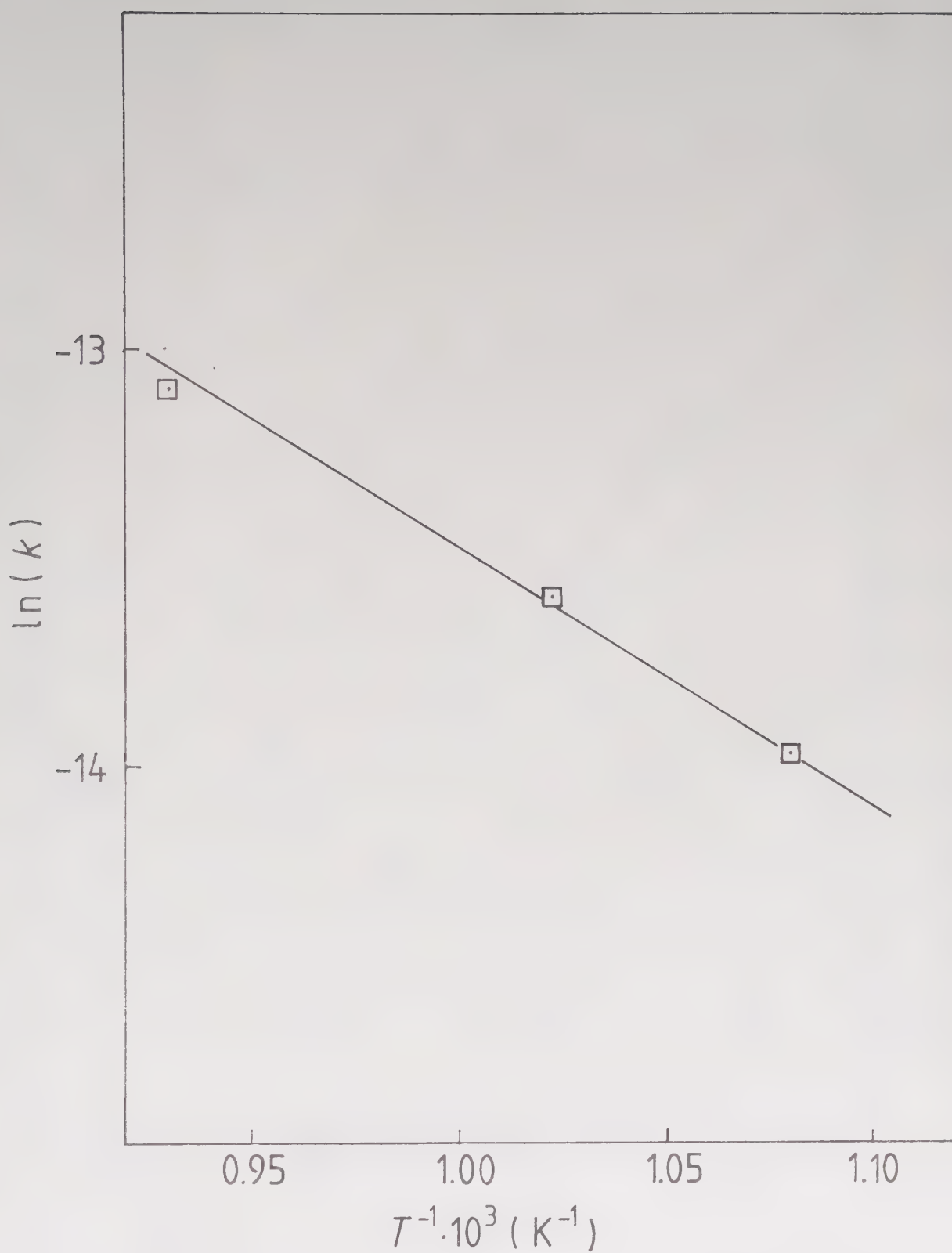


Figure 2.

Arrhenius plot, forward direction of the shift reaction over shale char.

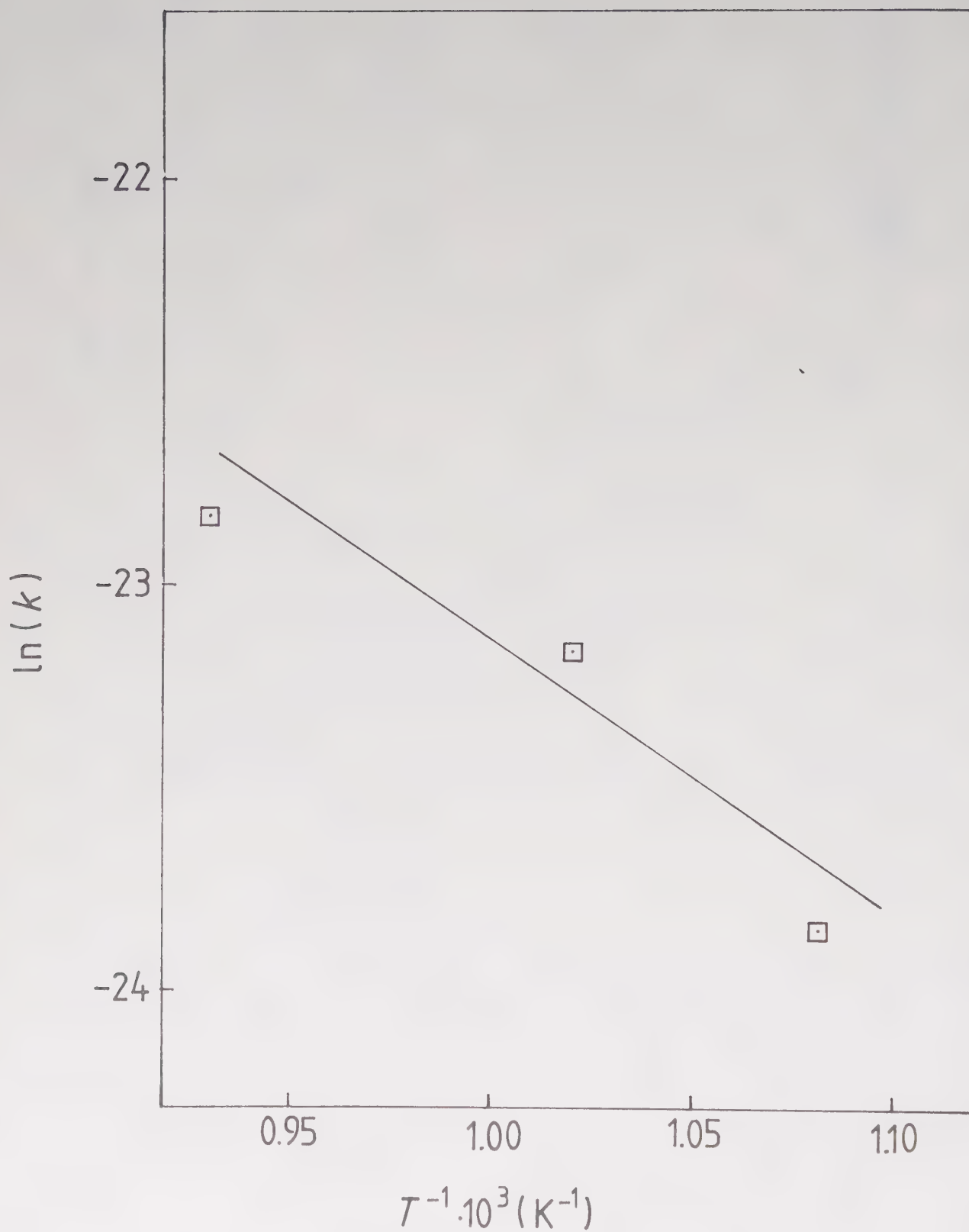


Figure 3.

Arrhenius plot, reverse direction of the shift reaction over shale char.

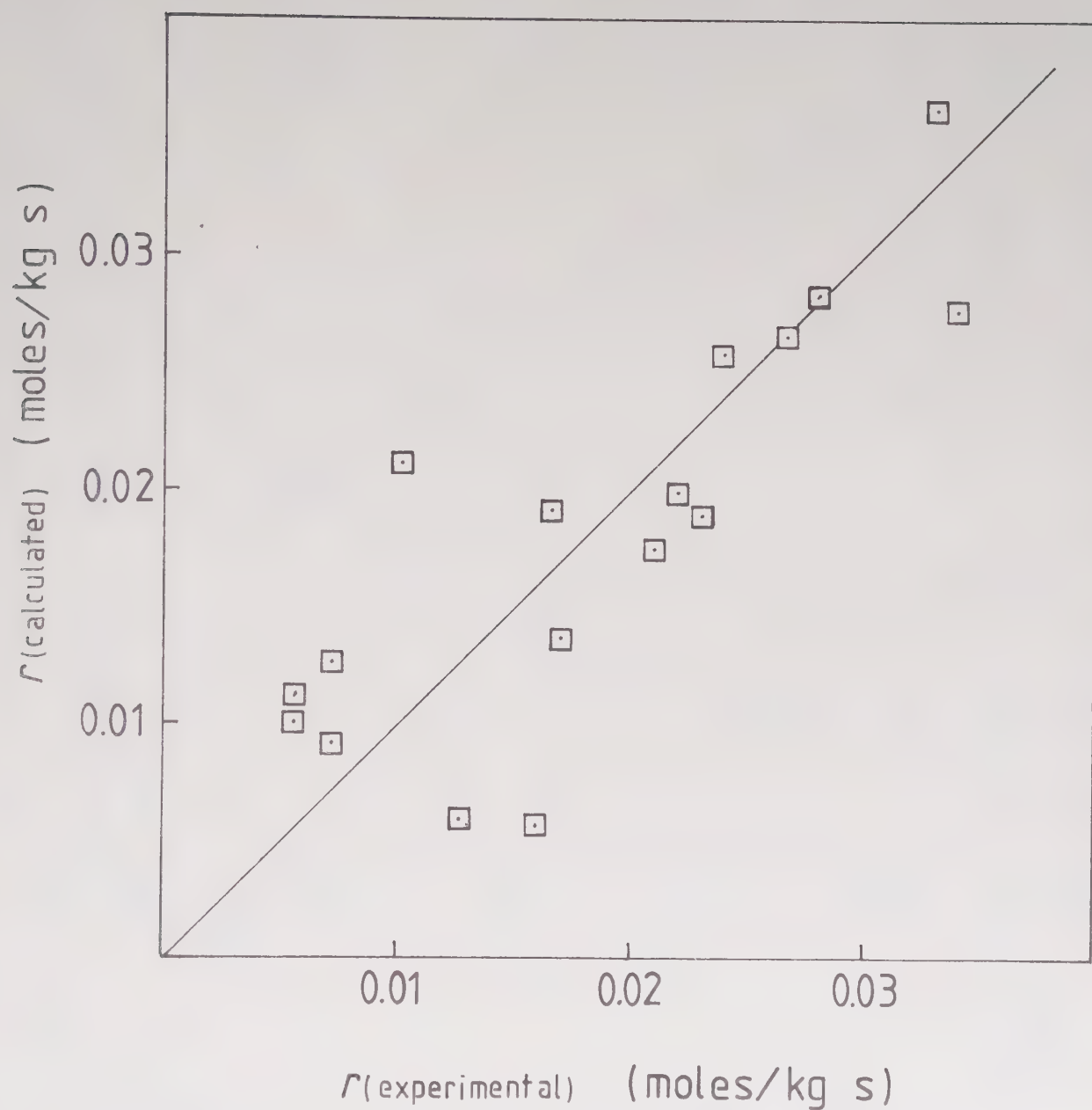


Figure 4.

Correlation of experimental and calculated reaction rates by the least-square fitting of the Langmuir-Hinshelwood equation (11).

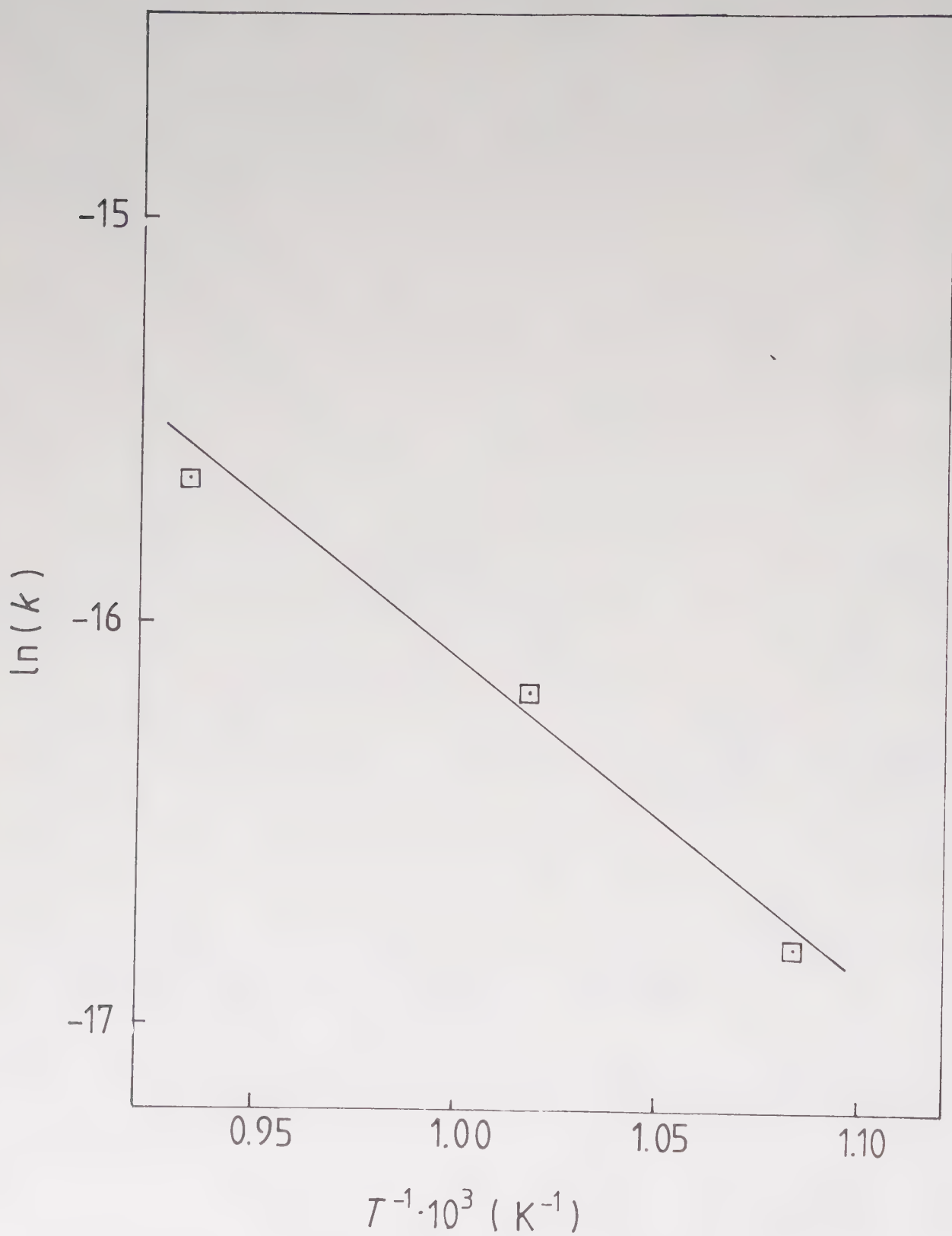


Figure 5.

Arrhenius plot, reverse direction of the shift reaction over kerogen free shale ash.

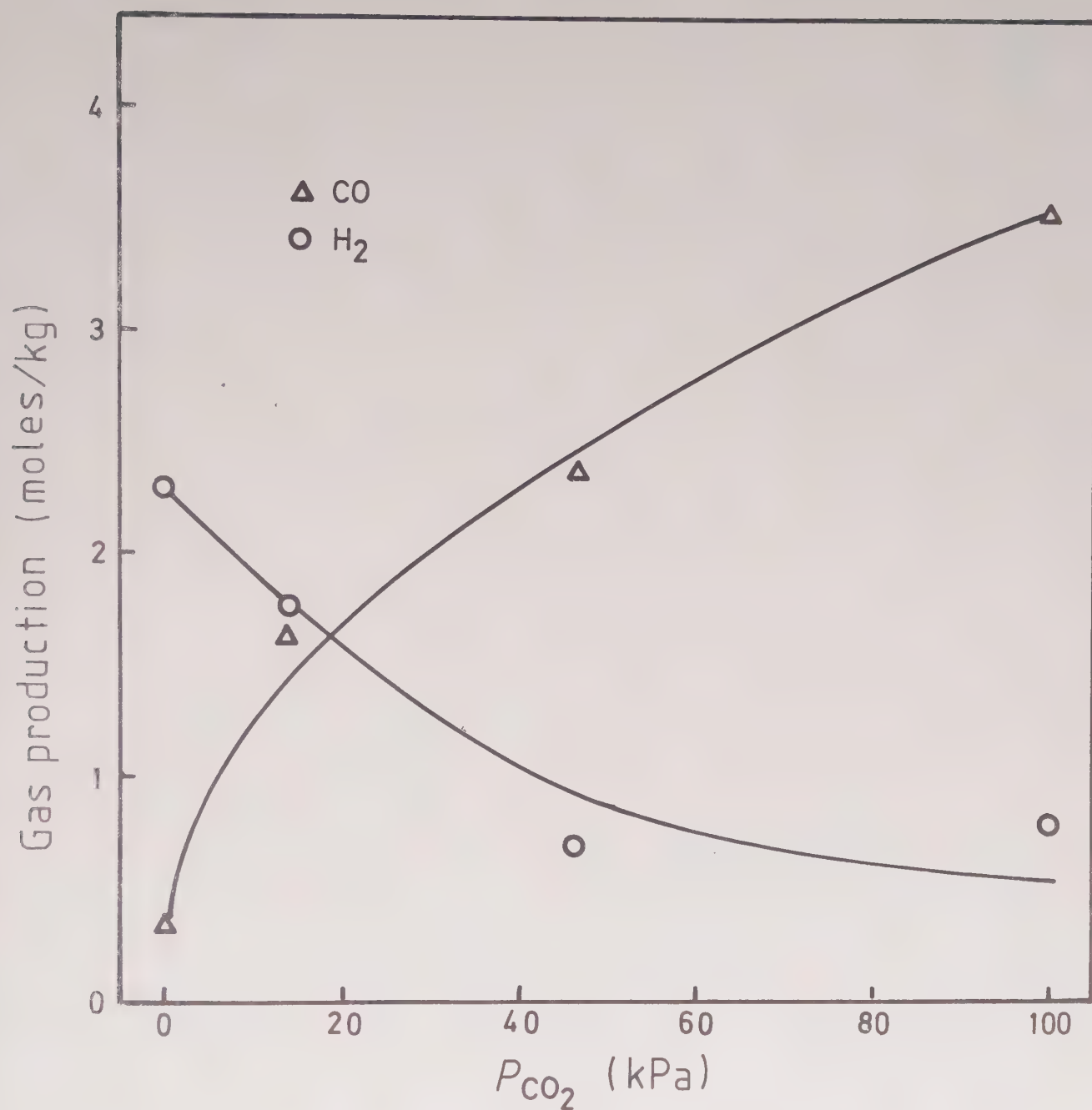


Figure 6.

Ranstad shale, CO_2 gasification, $800^\circ C$. Char residence time: 1 h.
Influence of the CO_2 partial pressure on the detected H_2 production.

A REACTOR MODEL FOR THE GASIFICATION OF BLACK
SHALE IN THE FLUIDIZED BED

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ABSTRACT

For scale-up and simulation calculations, a reactor model for an oxygen blown bubbling bed gasifier has been developed. Input data to the model are kinetic parameters for the fixed carbon gasification, shale feed rate, gasification temperature, reactor bed height and superficial gas velocity. The algorithm computes mass and energy balances, partial pressure profiles throughout the bed, shale and steam conversion and oxygen demand. The non ideal flow pattern of the gas phase is accounted for by an eddy diffusivity parameter. Due to the kinetic conditions of the fixed carbon gasification and the particle properties for the shale, an ordinary plug flow approximation for the gas phase was shown to give accurate results.

1. INTRODUCTION

An overwhelming part of the gasification processes presently being developed, use the fluidized bed principle for operation below the agglomeration point of the ash, while the entrained phase slagging principle is preferably used in the high temperature range. The fluidized bed offers a number of advantages over other types of low temperature reactors, such as moving or fixed beds; the capacity per unit can be considerably increased, the homogeneous and good temperature control allow operation close to the ash agglomeration temperature and the production of heavy by-products is diminished.

The disadvantages of the fluidized bed are, on the other hand, uncomplete carbon conversion, gas back mixing and, in some instances, poor gas/solid contact due to bubble cross flow. A very severe drawback is also the difficulty to predict reactor performance by scale-up. The last point makes development of fluidized bed processes more expensive than other concepts as the scale-up steps must be taken smaller. This is however in many cases only a half-truth, since the reasons for building pilot and demonstration plants are assigned to several other factors than only a check-up of the production rate and gas composition.

Research in the field of fluidized bed behaviour from both mechanistic and chemical points of view has been very intense over the last decades. A number of theories describing bubble behaviour, mass transfer resistance, and chemical kinetics, coupled with bubble hydrodynamics, have been developed, but none of them synthesize in a simple and handy way the effects of all these factors. The mechanistic studies of bubble behaviour are mostly conducted using idealized solids at ambient pressures and temperatures where no real processes are carried out. In analogy, investigations concentrating on chemical factors are often performed under conditions where fundamental fluidization properties cannot be observed or measured

The occurrence of gas bubbles in fluidized beds affect the reactor performance, from a chemical point of view, by primarily the following factors;

- o The gas back mixing lowers the reactant partial pressures at a given level. Product gas retardation effects occur at a lower bed-level compared with plug flow conditions.

- For fast reactions, the bubble cross flow gives low gas phase conversion, due to a mass transfer resistance between the bubble and solid phases.

2. FLUIDIZED BED REACTOR MODELS

In the following, some of the fluidized bed reactor models proposed in literature are to be reviewed in respect of their applicability to shale gasification.

One of the first reactor models to be developed was the two-phase model by May (1). The bed is assumed to consist of two phases, first, the suspension phase, consisting of the solids through which a gas flows at a rate corresponding to the minimum fluidization velocity, and secondly, the bubble phase. Between these phases, a mass transfer, characterized by a mass transfer coefficient takes place. For the bubble phase, plug flow is assumed, while the gas flowing through the suspension phase is back-mixed to an extent characterized by an axial dispersion coefficient. The model has been further improved by van Deemter (2), and van Swaaij and Zuiderweg (3), (4). Recently Werther (5, 6) extended the model in describing catalytic and non-catalytic reactions in fluidized beds. This model is especially designed to simulate catalytic processes, having very fine solids in deep beds, where the superficial gas velocity exceeds minimum fluidization by more than one magnitude. Later Davidson and Harrison (7) developed the bubble theory for gas/solid systems, using the analogy with gas/liquid systems.

Based on their conclusions Kunij and Levenspiel (8) presented the Bubble Model. The model describes the mass transfer from the bubble to the emulsion phase by coefficients obtained from the Higbie penetration theory. Beside observable or measurable physical properties, the model uses a "characteristic bubble diameter" as a central parameter, and here is one of the limitations of the model, how to define this bubble diameter for a given fluidized bed. Furthermore the model can only be used together with linear kinetics. This model has been slightly modified by Kato and Wen (9) in the Bubble Assemblage Model. They assume a stepwise increase of bubble diameter with bed height where each transfer unit of the bed

equals the bubble diameter at that bed level. This model is also only applicable to first order kinetics. An extensive correlation of gas/solid properties to operational modes of fluidized bed systems has been developed by Reh (10).

As a general conclusion, the academic fluidized bed research has been strongly directed towards fine solids fluidization applicable to catalytic gas phase reactions.

For the simulation of the shale gasification, a dispersion coefficient has been used to characterize the hydrodynamics of the fluidized bed. This approach can be considered as an approximation of the two-phase model in that the mass transfer coefficient for the bubble phase, together with the dispersion coefficient for the emulsion gas flow, have been replaced by a total eddy diffusivity characterizing both gas phases. The justification of this rather rough approach will be discussed from different points of view in the following.

A very important factor to take into consideration in fluidized bed modeling is the nature of the particles to be fluidized, e.g. the size, the density and the particle shape. A classification of solids with respect to their fluidization properties has been presented by Geldart (11). He concludes the mass transfer conditions, e.g. the cross flow by the bubble phase to be greatest for fine particles, 20 to 100 micrometer in diameter. With these particles superficial fluidizing velocities exceeding the minimum fluidization conditions by a factor 10 to 100 are often used. Thus, only a minor part of the total gas flow passes the emulsion phase. Additionally, these particles can keep large gas volumes imbibed in the bed by the development of a laminar gas film around the individual particle. This effect can be easily observed by suddenly shutting off the gas flow to the bed, which returns to the fixed bed status first after several seconds, when all the imbibed gas has been given off. For obvious reasons, neglecting the bubble mass transfer in this case will be disastrous. However, due to the particle sizes used, and the density of the shale particles, the shale falls into a group of particles called "sandy" by Geldart. The coarseness and the large density of these particles give high

minimum fluidization velocities, no laminar gas films around the particle and superficial velocities differing from the minimum fluidization velocity by a factor below 10, (in the shale case 1.5 - 3). This implies that a considerable fraction of the total gas flow passes the bed in the emulsion phase giving a good gas/solid contact.

The degree of dispersion, e.g. the deviation from plug flow is strongly dependent of the particle sizes and gas velocities used. Park et al. (12) conclude the plug flow model to be the most correct approximation of a fluidized bed with solid phase characteristics similar to the shale case. Thus, the two-phase models do not apply to these systems. Additionally, the inter phase resistance between the bubble and emulsion phases occurs when the kinetic reaction rate is exceeding the mass transfer process. Due to the slowness of the gasification reactions and the physical properties of the char it is probable to assume the influence of a bubble phase resistance to be of minor importance.

3. APPLICATION OF THE GAS PHASE DISPERSION MODEL TO BLACK SHALE GASIFICATION IN AN OXYGEN BLOWN BUBBLING BED GASIFIER.

3.1 KINETIC DATA BASE

The kinetic base data used in the reactor model have been obtained by bench scale tests and thermogravimetric investigations. These studies are thoroughly reported in the references (13, 14, 15), and here the findings should be shortly overviewed. The following reaction steps are involved in the gasification model.

- o Fixed carbon gasification
- o Shift conversion
- o Pyrolysis and sulfur reactions

To start with the fixed carbon reactions, the gasification of carbon is expressed by the equation(1), with the kinetic parameters given in (14).

$$-(r_C) = \left(k_1 \frac{k_2 P_{H_2O}}{1 + k_2 P_{H_2O} + k_3 P_{H_2} + k_3^{-0.25} P_{CO}} + k_4 \frac{k_5 P_{CO_2}}{1 + k_5 P_{CO_2} + k_6 P_{CO}^{0.05} + k_6^{-1} P_{H_2}} \right) c_C \quad (1)$$

For the shift reaction, the equation 2 with data from (15) is used,

$$r_{CO_2} = \frac{k_7 (P_{H_2O} P_{CO} - k_8 P_{H_2} P_{CO_2})}{1 + K_{H_2O} P_{H_2O} + K_{CO} P_{CO} + K_{H_2} P_{H_2} + K_{CO_2} P_{CO_2}} \quad (2)$$

The kinetic conditions for the hydrocarbon and sulfur devolatilization reactions have not been investigated in deep. The production of these species in the model is based on gas analyses from the fluidized bed tests reported in (13). In the model all hydrocarbons are expressed as methane, which is the major constituent of the pyrolysis products. These yields are almost unaffected by gasification temperature and char residence time, and have therefore been assumed constant in all the simulations.

3.2. DESCRIPTION OF THE MODEL

The reactor model developed is aiming at a description of an oxygen blown bubbling fluidized bed gasifier as shown in Figure 1. The most important assumptions about the reactor behaviour are listed below.

- o Complete backmixing of the solid phase
- o Isothermal conditions throughout the bed
- o The pyrolysis process takes place uniformly within the whole bed volume.
- o Oxygen reacts only with gaseous compounds in the lower section of the bed. The combustion rate is assumed instantaneous with the gas production, given by the gasification and pyrolysis reactions, being the rate controlling step.
- o The gas phase is assumed to be backmixed. This phenomena is described by an axial dispersion coefficient.

In the model, mass and heat balances, solid phase conversion, partial pressure profiles in the vertical direction of the bed and oxygen demand are calculated. Input data to the calculations are shale feed rate, superficial gas velocity in the bottom increment, gasification temperature and temperatures of the shale, and oxygen and steam feed flows.

In the model, the gas phase can either be considered to follow the plug flow model or be backmixed.

The calculation of the vertical pressure profiles in the bed is done by an iterative procedure. For simulations including the backmixing a simple step by step calculation is not possible because the gas composition in the subsequent increment upwards in the bed must be known. A mass balance for an increment, where the previous situation is shown, is given in Figure 2. The calculation is therefore first done without gas backmixing which yields good initial values for the iterative calculations involving gas dispersion. In the simulations eddy diffusivities up to $50 \text{ m}^2/\text{s}$ have been used. Investigations on gas backmixing in fluidized beds of fine solids summarized in (17) gave maximum values of $0.5 \text{ m}^2/\text{s}$. Defining a dispersion parameter as

$$\gamma = \frac{E}{v \cdot H_{\text{tot}}} \quad (3)$$

yields values for the literature data in the order of 1 to 3, while in the simulations a maximum dispersion parameter of 10 was used. This value is very high, especially when considering the difference in gas flow pattern in fluidized beds of fine and coarse particles mentioned in section 2. Here the much higher degree of backmixing for fine particles was stated.

The gas composition within the increment is assumed uniform, e g completely backmixed. Since the calculations have been performed with increment heights of only 0.1 m this will, due to the slow reaction rate of the fixed carbon gasification, have a limited impact on the results. Due to the complexity of the kinetic equations, the gas composition within each increment is calculated iteratively. A simplified flowsheet of the computer algorithm is shown in Figure 3.

4. RESULTS

In the forthcoming, first the accuracy of the model to predict the performance of a pilot plant gasifier will be outlined. Secondly, scale-up simulations of a commercial scale reactor are presented.

As pointed out in section 2 and 3.2, the reactor model uses an eddy diffusivity to describe the gas backmixing. Simulations with values of the dispersion up to $50 \text{ m}^2/\text{s}$ corresponding to a high degree of backmixing showed a very slight influence of dispersion on the reactor model outputs. A comparison of the plug flow approximation with the calculations including dispersion is shown in Figure 4. Because of this result, the simulations of the pilot plant data and the scale-up calculations are all done with the plug flow model for the gas phase.

4.1 COMPARISON OF MODEL OUTPUT WITH PILOT PLANT DATA.

For a test of the accuracy of the reactor model, data from the oxygen blown pilot plant gasifier, operated by Ranstad Skifferaktiebolag at Ranstad, have been used. This reactor is 0.4 m in diameter with bed heights ranging from 1.5 to 3.5 m. Six different experiments with temperatures between 807 and 947 °C have been simulated. All runs were conducted with constant char residence time, bed height and superficial gas velocity of 0.9 h, 1.6 m and 0.5 m/s respectively. The tests were selected from about 100 runs, with the objective to use runs carried out at true steady state, balanced mass and heat flows and negligible axial temperature gradient in the bed.

In Figure 5 the experimental and simulated carbon conversions and gasification efficiencies are shown. The corresponding gas compositions are displayed in Table 1. The quite good agreement between the measured and calculated results can be stated. This is also an indication of the correctness of the assumptions made about the combustion reactions and the gas phase hydrodynamics. The validity of the plug flow approximation seems quite consistent for the pilot reactor, based firstly on the literature findings, referred to earlier (12), but also on the geometry of the reactor with a bed height to diameter ratio of 4 to 9, depending on bed height chosen. In a larger scale with larger bed diameters the radial conditions are naturally different with another flow pattern and growth rate for the bubbles. This will certainly influence the performance, but due to

the form of the kinetic equations, the influence should be small.

To test the assumption about the combustion reaction, e.g. the oxygen reacts only with gases produced by pyrolysis and gasification, simulations assuming exclusively fixed carbon combustion were made. This approach showed a nonconsistency with the experiments in that both the carbon conversion and the gasification efficiency was considerably overestimated by the model.

In summary, the reactor model is able to predict the performance of the pilot plant gasifier and the assumptions made in the model were shown to be reliable.

4.2 SCALE-UP PREDICTIONS

The scale-up calculations have been performed for a reactor with an effective bed height of 5 m. The calculations are based on a unit cross-sectional area but this approximation will not be too severe, as pointed out in section 4.1. The range of the process parameters varied are summarized below.

- Temperature 800 to 950 °C.
- Char residence time 1 to 4 hours.
- Superficial gas velocity at the gas distributor 0.5 and 1 m/s.
- Shale feed temperature 0 °C.
- Gas feed temperatures, steam 500 °C, oxygen 300 °C.

In Figure 6. the gasification efficiency is shown as a function of temperature, with gas velocity and char residence time as parameters. The figure only summarizes the technically interesting cases, whereas some of the less realistic simulations are discussed below.

At high temperature, 950 °C, 1 h char residence time and 0.5 m/s superficial gas velocity, the high shale load and the low gas velocity lead to a feed gas composition consisting of pure oxygen. This situation is technically impossible to operate due to immediate agglomeration of the char at the oxygen inlet.

Char residence times lower than 1 h are also less interesting, since due to the high shale load either low gasification temperatures are obtained, or almost pure oxygen must be fed to the reactor, even at the maximum gas

velocity of 1 m/s.

Looking at Figure 6 it can be seen that considerable benefits are won by increasing the gas velocity from 0.5 to 1 m/s for the 2 h residence time runs. Although an increased part of the shale is used for heating the additional steam, the effects of a larger driving force for the gasification reactions due to lower steam conversion promotes the gasification efficiency. The inhibitative effects of carbon monoxide and hydrogen are also diminished.

Furthermore, by using longer char residence time (4 h), an acceptable gasification efficiency can be maintained at lower temperatures compared with the the other cases. In this respect, the increased investment in a larger reactor must be judged against the benefits of a better shale utilization.

In conclusion, to obtain good efficiencies, the reactor should be operated at highest possible temperature and gas velocities of 1 m/s at the shorter residence times of 1 and 2 hours. At longer residence time, lower temperature and gas velocities give acceptable gasification efficiencies. It can further be stated that an increased shale feed rate decreases the efficiency considerably, but simultaneously the energy content of the gas produced per unit reactor area will increase as shown in Figure 7 for a temperature of 900 °C and 1 m/s gas velocity.

In Table 2 gas compositions and carbon conversions for some combinations of parameters are shown. The gas produced at high temperatures has a high content of carbon monoxide and hydrogen. After sulfur removal this gas is suitable for synthesis gas production.

Table 3 displays the oxygen consumption related to output of chemical energy as gas. At low temperature the oxygen demand per kg of shale feed is low, but the slowness of the gasification reactions leads to a poor gas production per kg of oxygen.

At higher temperatures, e g 900 - 950 °C, the situation is opposite. The specific oxygen demand is high, but the yield of chemical energy in gas is about 50 % higher than for the 800 °C case.

5. CONCLUSIONS

The reactor model presented has been able to simulate experimental results from a pilot plant gasifier. The plug flow model could be used to describe the gas phase hydrodynamics because of the kinetic conditions for the fixed carbon gasification and the physical properties of the char particles.

Using the model for scale-up calculations demonstrated that to achieve acceptable gasification efficiencies, temperatures above 850 °C and residence times of 2 hours or more, are necessary.

ACKNOWLEDGMENT

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NOTATION

- C = Conversion factor between partial pressure and concentration ($\text{mole/m}^3, \text{Pa}$)
E = Eddy diffusivity (m^2/s)
H = Height of one increment (m)
 H_{tot} = Total bed height (m)
I = Increment index
J = Gas component index
 k_1, k_4 = Constants ($1/\text{s}$)
 k_2, k_3, k_5, k_6 = Constants ($1/\text{Pa}$)
 k_3^- = Constant ($1/\text{Pa}^{0.25}$)
 k_6 = Constant ($1/\text{Pa}^{0.05}$)
 k_7 = Constant (mole/kg, s, Pa^2)
 k_8 = Constant (dimensionless)
 $K_{\text{H}_2\text{O}}, K_{\text{CO}_2}, K_{\text{CO}}, K_{\text{H}_2}$ = Constants ($1/\text{Pa}$)
 $P, P_{\text{H}_2\text{O}}, P_{\text{CO}_2}, P_{\text{CO}}, P_{\text{H}_2}$ = Partial pressure (Pa)
R = Production rate (mole/s)
 r_{C} = Reaction rate of fixed carbon (mole/kg, s)
 r_{CO_2} = Reaction rate of CO_2 in shift reaction (mole/kg, s)
V = Gas volume flow (m^3/s)
v = Superficial gas velocity (m/s)

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Table 1. Comparison, pilot plant data - reactor model output.

T (°C)		Gas composition (vol-%)					
		H ₂ O	CO ₂	CO	H ₂	CH ₄	H ₂ S
807	M	57.7	19.4	3.2	11.3	3.8	4.0
	C	64.7	12.6	3.4	11.6	2.9	2.8
808	M	58.6	20.0	3.0	10.7	3.6	3.5
	C	61.1	12.9	4.0	13.1	3.5	3.3
899	M	46.4	17.6	10.1	18.9	2.7	3.5
	C	37.8	20.5	13.2	20.7	3.6	3.4
900	M	31.0	27.3	11.5	19.5	4.3	5.7
	C	36.0	20.5	14.3	20.7	3.8	3.6
946	M	33.1	22.8	14.1	21.8	3.3	4.6
	G	27.9	21.5	20.8	21.9	3.7	3.5
947	M	32.8	22.7	15.2	20.8	3.3	4.9
	C	28.3	22.6	20.1	21.1	3.7	3.5

M = Measured

C = Calculated

Table 2. Data for some of the scale-up simulations.

T (°C)	950	950	850	850	800
v ₀ (m/s)	1	1	1	1	1
Res.time (h)	2	1	4	2	2
Gas comp.(vol-%)					
H ₂	34.6	29.2	40.9	37.4	36.6
CO	28.9	36.2	12.5	15.7	9.7
CO ₂	26.9	21.4	38.3	33.9	36.0
CH ₄	4.5	6.2	4.2	5.8	7.1
H ₂ S	4.3	5.9	4.0	5.5	6.7
Gross heat of comb.(MJ/Nm ³)	11.0	12.3	9.5	10.5	10.4
Carbon conv. (%)	85.0	64.8	73.5	53.9	34.1
Gasification efficiency (%)	63.3	50.6	51.5	42.0	28.1

Table 3. Oxygen consumption at various operating conditions.

T (°C)	Res. time (h)	Superficial gas velocity (m/s)	Oxygen demand	
			kg/kg shale feed	kg/GJ chemical energy in gas
800	4	1	0.15	65.3
850	4	1	0.177	52.0
900	4	1	0.197	48.7
800	4	0.5	0.121	51.8
850	4	0.5	0.146	43.8
900	4	0.5	0.167	41.3
800	2	1	0.116	62.4
850	2	1	0.137	49.4
900	2	1	0.159	44.1
950	2	1	0.178	42.7
800	2	0.5	0.099	54.8
850	2	0.5	0.117	46.1
900	2	0.5	0.137	42.3
950	2	0.5	0.155	41.7
800	1	1	0.094	63.2
850	1	1	0.109	50.3
900	1	1	0.128	45.5
950	1	1	0.145	43.3

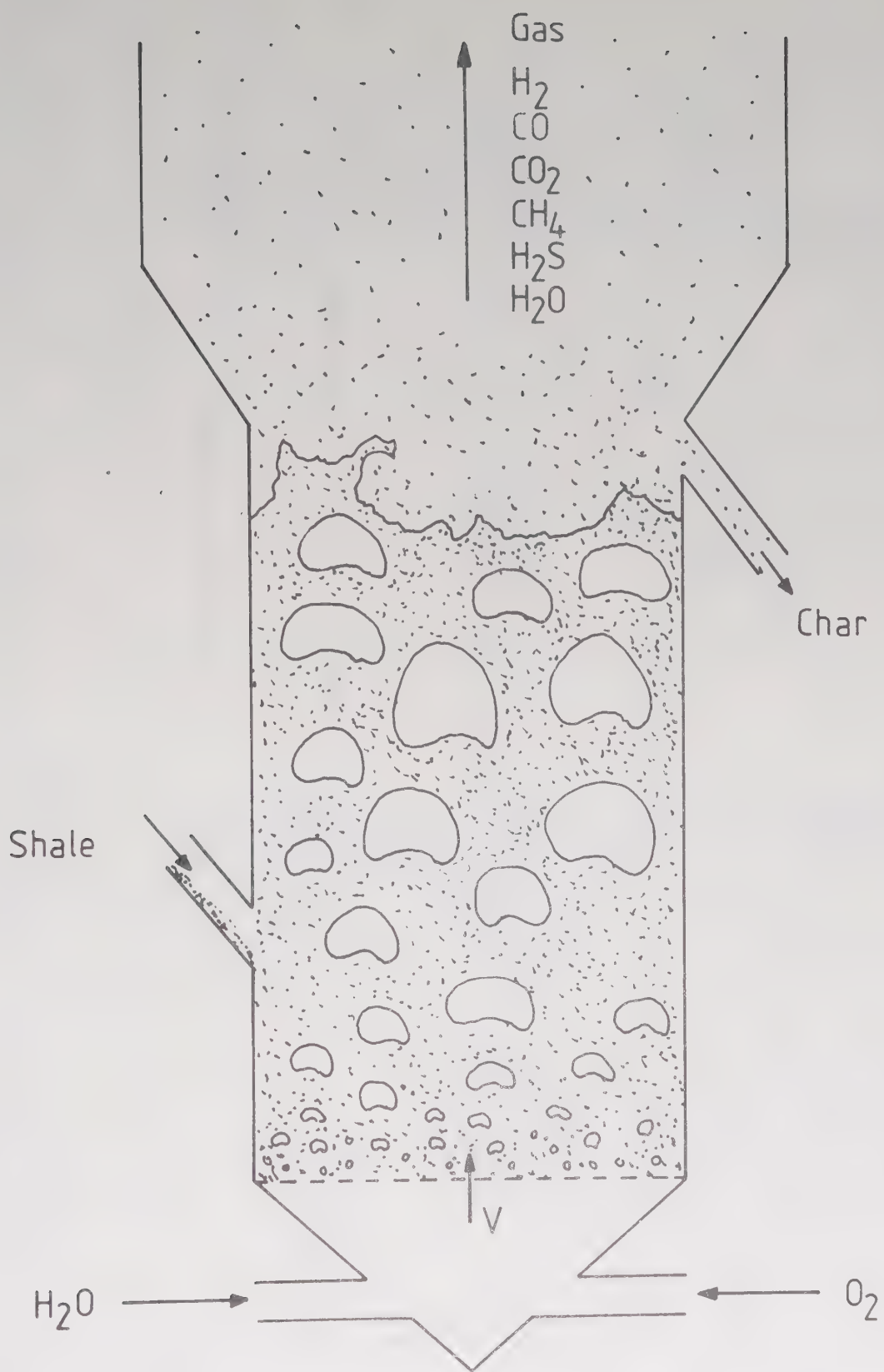


Figure 1

Reactor concept to be described by the model.

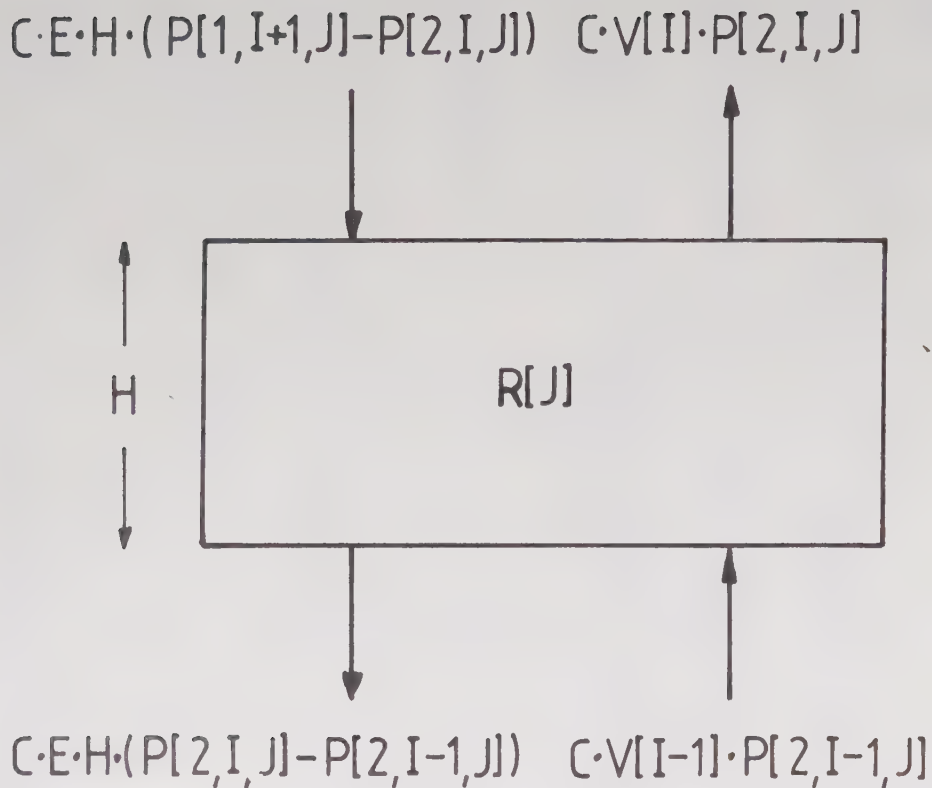


Figure 2

Mass balance for an incremental height unit.

E = Eddy diffusivity (m^2/s)

H = Height of increment (m)

V = Volumetric gas flow (m^3/s)

P = Partial pressure (Pa)

R = Production term (mole/s)

C = Conversion factor between concentration and partial pressure (mole/Pa, m^3)

Indexes: I = Increment no

J = Gas component

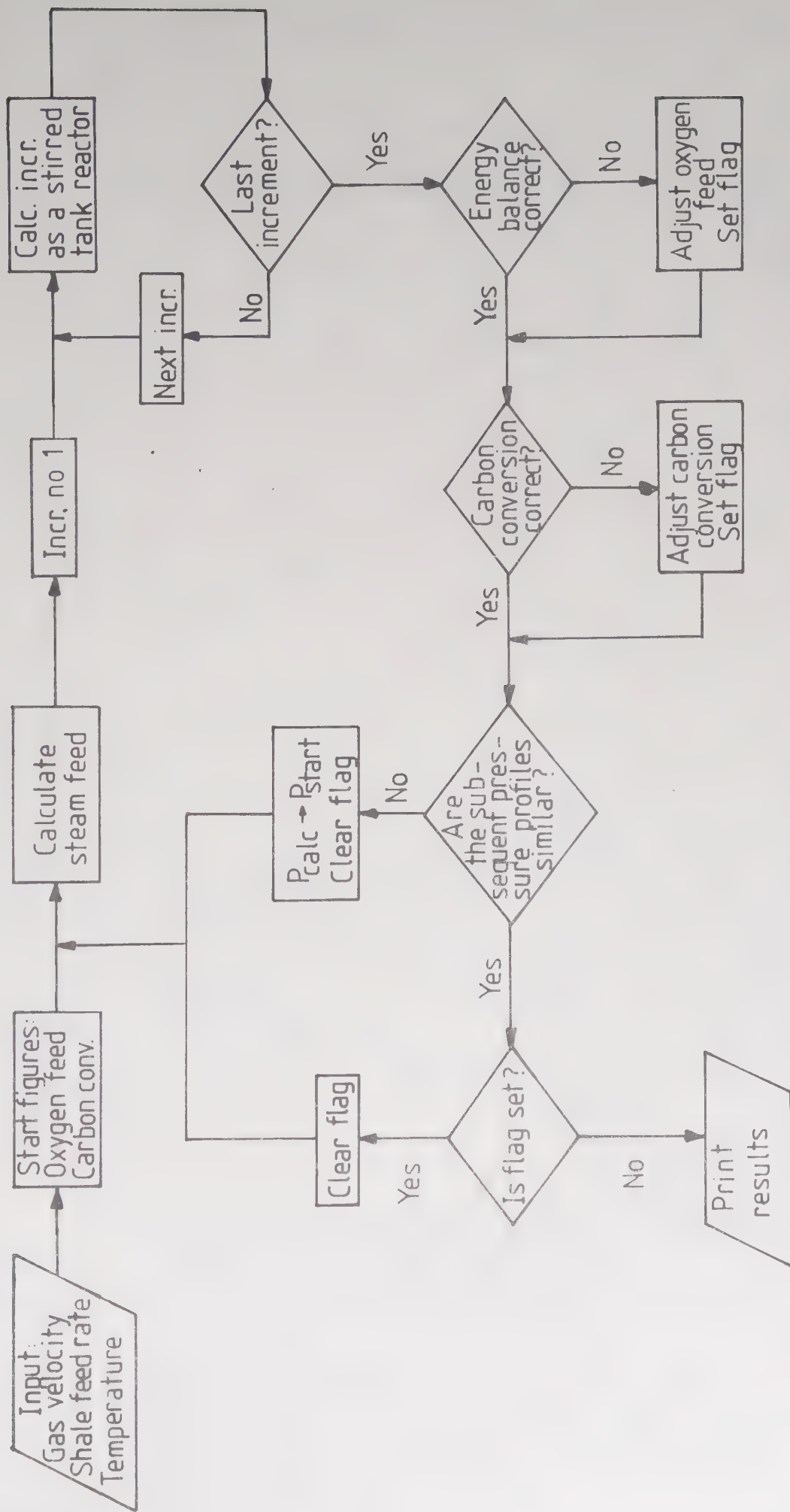


Figure 3
Flowsheet for the reactor model algorithm.

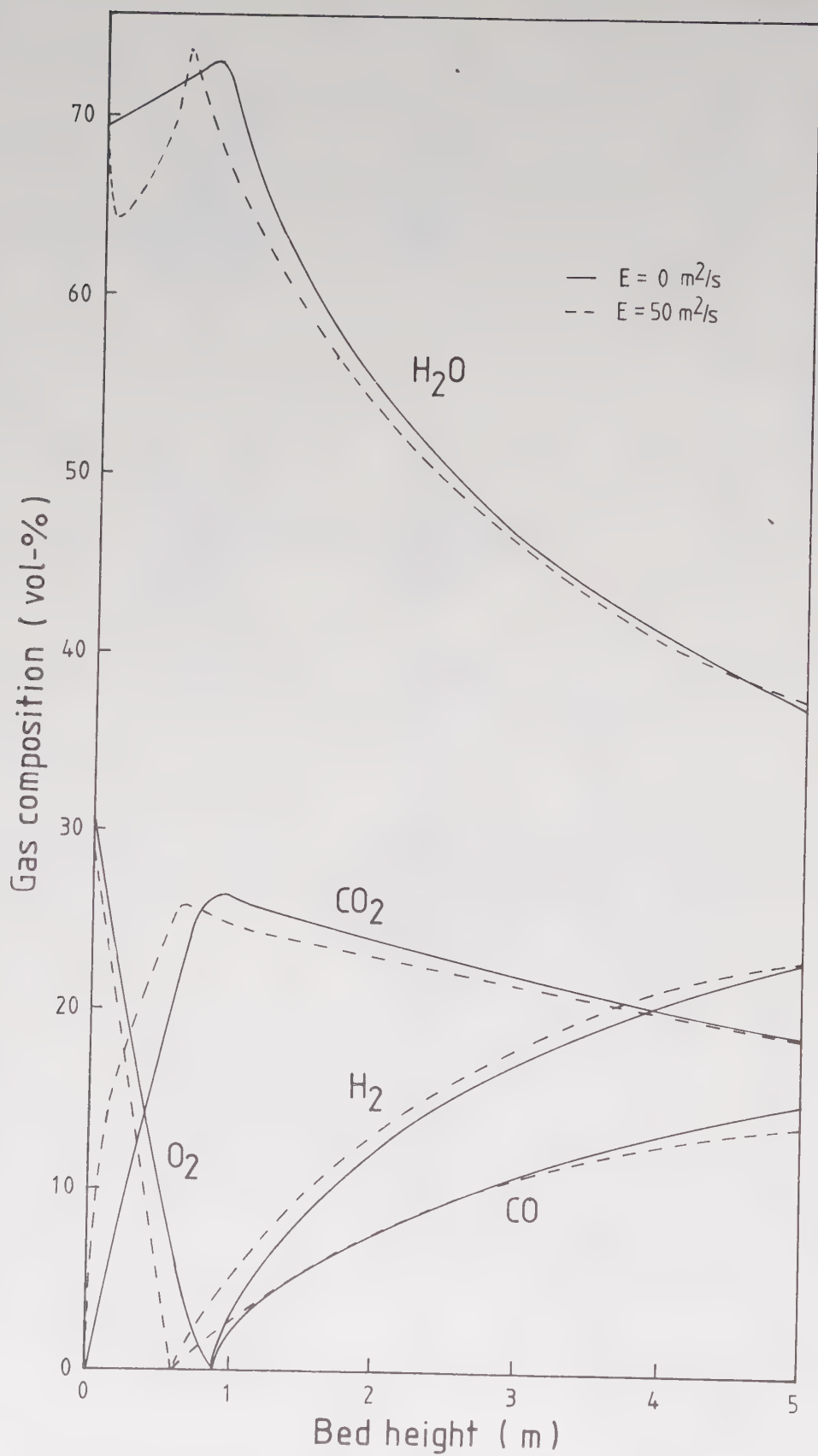


Figure 4

Comparison of partial pressure profiles with and without gas dispersion

Gasification temperature 900°C

Superficial gas velocity 1 m/s

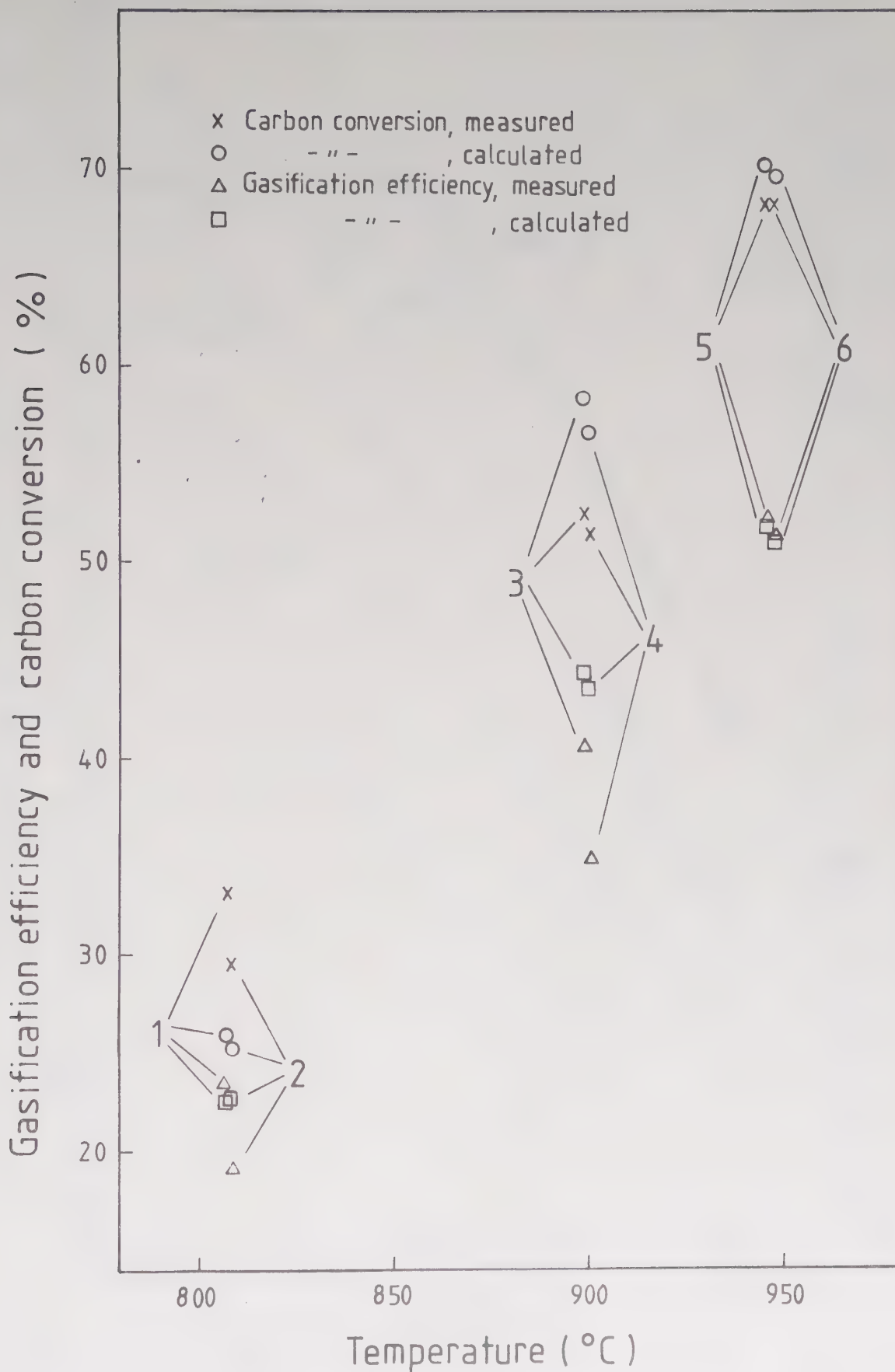


Figure 5

Comparison of reactor model results with pilot plant data. Gasification efficiency and carbon conversion as a function of temperature.

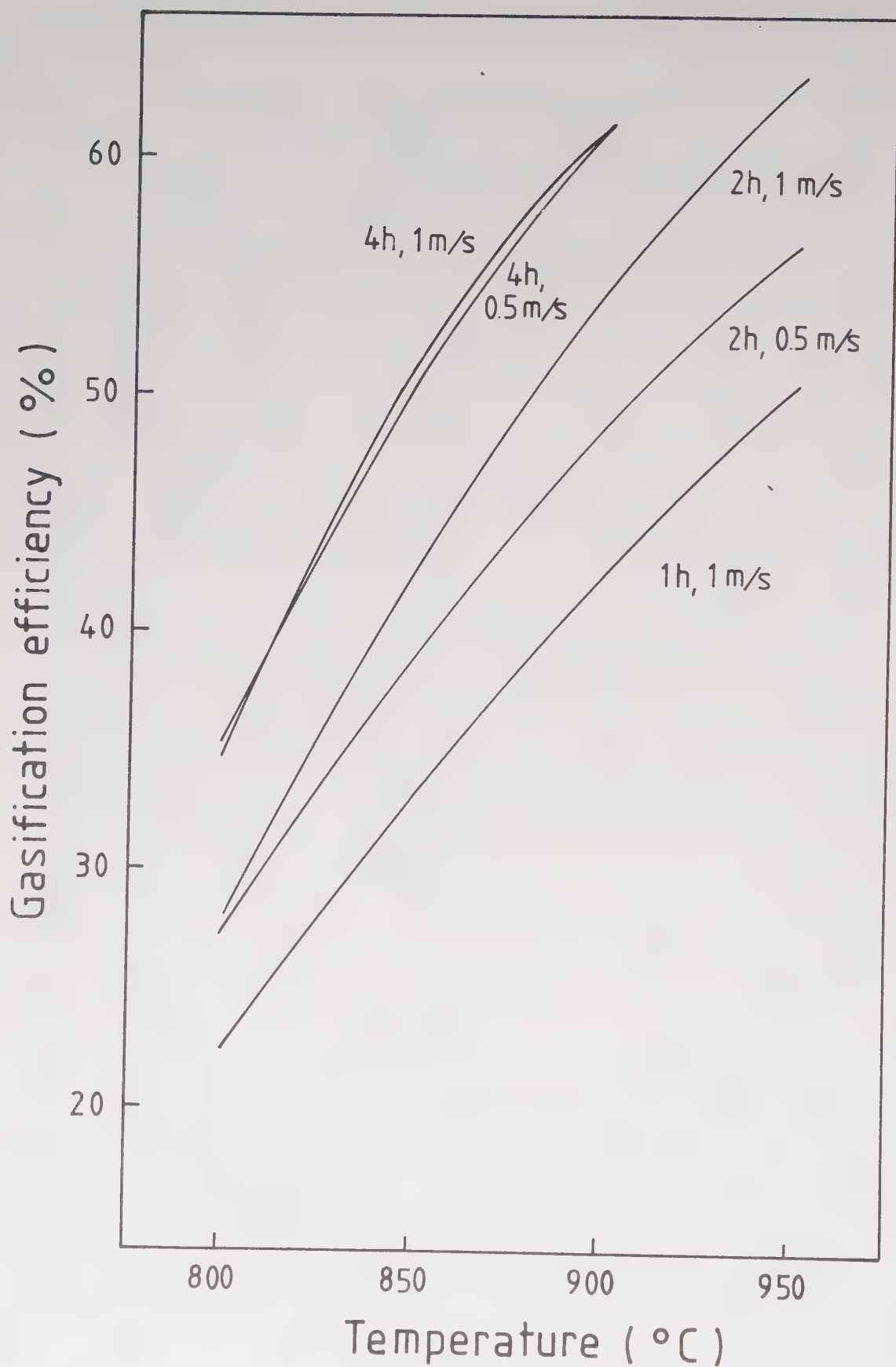


Figure 6

Scale-up calculations. Gasification efficiency as a function of temperature with char residence time and superficial gas velocity as parameters.

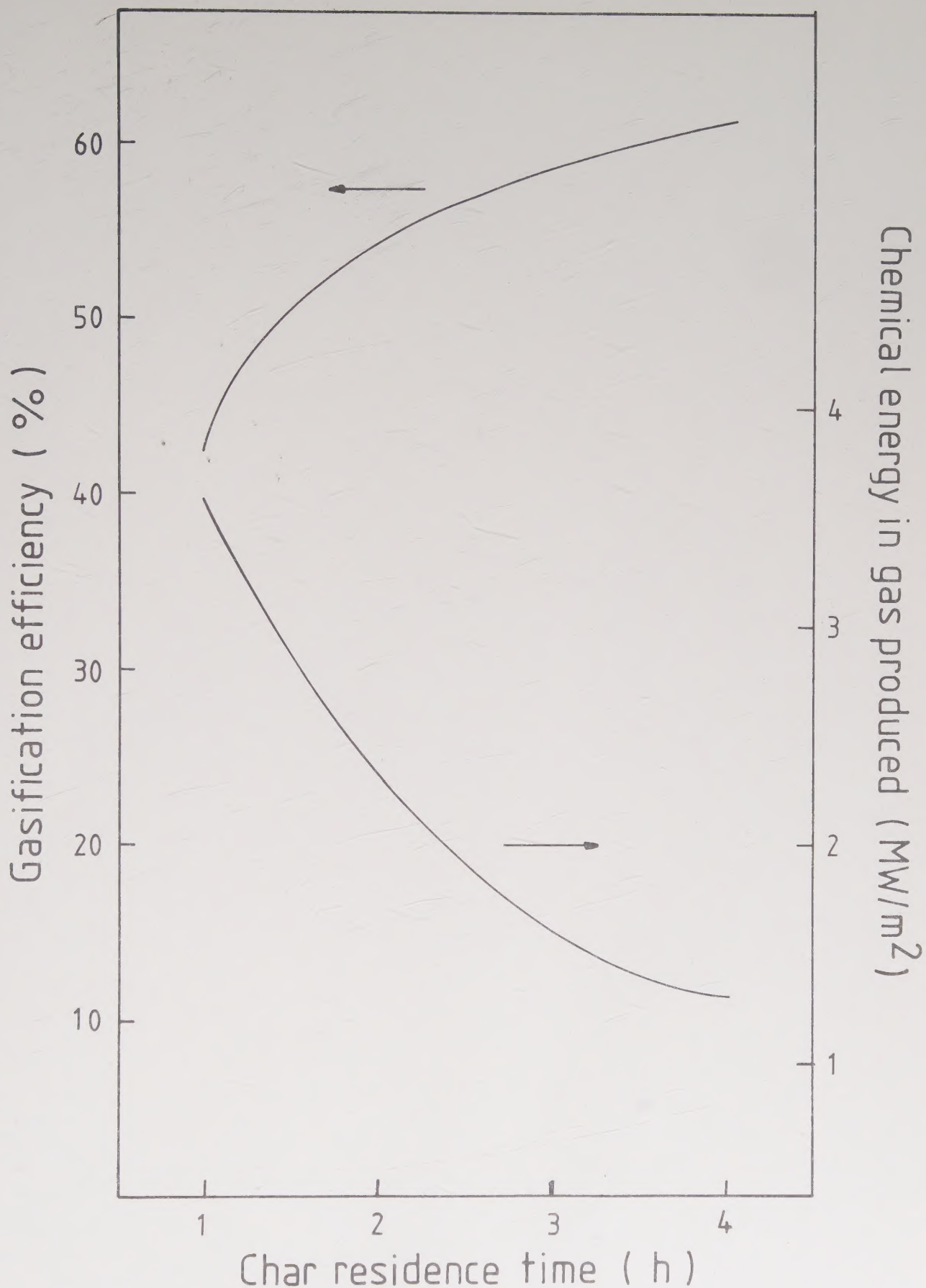


Figure 7

Scale-up calculations. Specific production of chemical energy in gas and gasification efficiency as a function of char residence time. Temperature 900 °C, gas velocity 1 m/s.

